SPECTROSCOPIC STUDIES OF PLATINUM HALO-PHOSPHINE COMPLEXES.

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To my wife Jan, with love.

DECLARATION.

This dissertation has not been submitted, in whole or in part, for any degree at this or any other university. Preliminary work to the results described in chapter 3 was carried out by Mr.B.Turner as part of a chemistry IV project. Further work on this was carried out by Prof.C.W.Allen on sabatical leave from the University of Vermont. All reactions reported herein were carried out by me under the direction of my supervisors Prof.E.A.V.Ebsworth and Dr.D.W.H.Rankin. Where this is not so, credit has been duly given.

CONTENTS.

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To my many friends and colleagues, past and present, in the inorganic research group who shared the ups and downs, my warmest thanks are offered.

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Last, and by no means least, I thank my wife Jan for her patience and understanding throughout the course of this work.

ABSTRACT.

This thesis descibes n.m.r. spectroscopic studies of the preparation and reactions of some platinum(II) halo-phosphine and phosphane species. $PtClH(PEt_3)_2$ reacts with PCl_3 in CD_2Cl_2 at 180 K to produce $PtCl(PEt_3)_2(PCl_2)$. On warming the solution, reversible protonation occurs to give $[PtCl(PEt_3)_2(PCl_2H)]^+$. Further warming of the solution results in the formation of $PtCl(PEt_3)_2(PH_2Cl_2)$. This species is thermally unstable above 260 K. Reaction of this species with HCl or BCl_3 results in its dissociation to $PtCl(PEt_3)_2(PH_2Cl)$ and HCl_2 or $[BCl_4]^-$. Analogous behaviour was observed in the reaction of $PtBrH(PEt_3)_2$ with PBr_3 except that the initial six-coordinate product of oxidative addition at platinum was detected. The mechanism of formation of these products is discussed.

Isolation of $PtCl(PEt_3)_2(PCl_2)$ as an oil from the reaction of $PtClH(PEt_3)_2$ with PCl_3 in the presence of Me_3N allowed its chemistry to be studied. A wide range of reactions was carried out with non-transition metal species to produce several interesting products. Reactions with transition metal complexes resulted in the formation of several hetero and homo-bimetallic species containing $-PCl_2$ or -PCl bridging groups.

Attempts were made to produce a species containing a terminal $-PF_2$ group by the reaction of $PtH_2(PCy_3)_2$ with difluorophosphine species. Although unsucessful, the resulting cationic species contained $-PF_2H$ groups and

were spectroscopically characterised.

An appendix containing n.m.r. parameters for complexes of iridium, platinum and rhodium is also included.

CHAPTER 1

INTRODUCTION

This chapter will give a brief discussion of the chemistry and techniques relevant to the remainder of this work.

1.1. The chemistry of platinum.

Platinum was present at the birth of organometallic chemistry in 1830 when the Danish pharmacist Zeise boiled potassium hexachloroplatinate(IV) in ethanol[1] and so produced yellow crystals of $K^+[Pt(C_2H_4)Cl_3]^-.H_2O$ - now known as Zeise's salt. From this time to the present, platinum has played an important role in organometallic and coordination chemistry, forming a wide range of kinetically stable complexes. Increasingly, the stability of a complex has become less important to its characterisation as modern spectroscopic techniques, particularly nuclear magnetic resonance spectroscopy, have facilitated the study of unstable species and species formed as short lived intermediates in the course of a reaction.

The compounds of platinum show a strong preference for three oxidation states - 0, +2 and +4. Although the +1 state is becoming more widely reported, the +3 and +5 states are very rare and the +6 state is only found when the platinum is surrounded by highly electronegative ligands such as fluorine or oxygen as in PtF_6. The only negative oxidation states of platinum occur in polynuclear carbonyl anions which have aroused interest in the hope that carbonyl clusters may be useful as catalysts.[2]

The recognition of square-planar geometry in compounds of the +2 oxidation state (square pyramidal geometry is also known) opened up the possibility of cis-trans-isomerisation in such complexes. From this followed the discovery of the "trans effect" in platinum(II) complexes in the 1930's.[3] This resulted in the systematic synthesis of many novel platinum(II) complexes. The vast number of organometallic compounds of platinum which have been synthesised reflects the interest in their varied applications. The field of homogeneous catalysis in the reactions of organic compounds has produced several commercially important reactions. Extensive studies have provided some basis for a discussion of the mechanism of organic reactions catalysed both by the metal itself and by a wide range of its complexes.

Platinum(II) can be regarded as a Class b metal under Chatt's scheme[4] or as a soft acid under Pearson's scheme.[5] Both classifications indicate that platinum forms halide complexes in decreasing order of stability $I^- > Br^- > Cl^- >> F^-$. This preference is exploited in the halogen metathesis reactions[6] utilised in chapter 2.

$$PtClH(PEt_3)_2 + NaX \rightarrow PtHX(PEt_3)_2 + NaCl$$

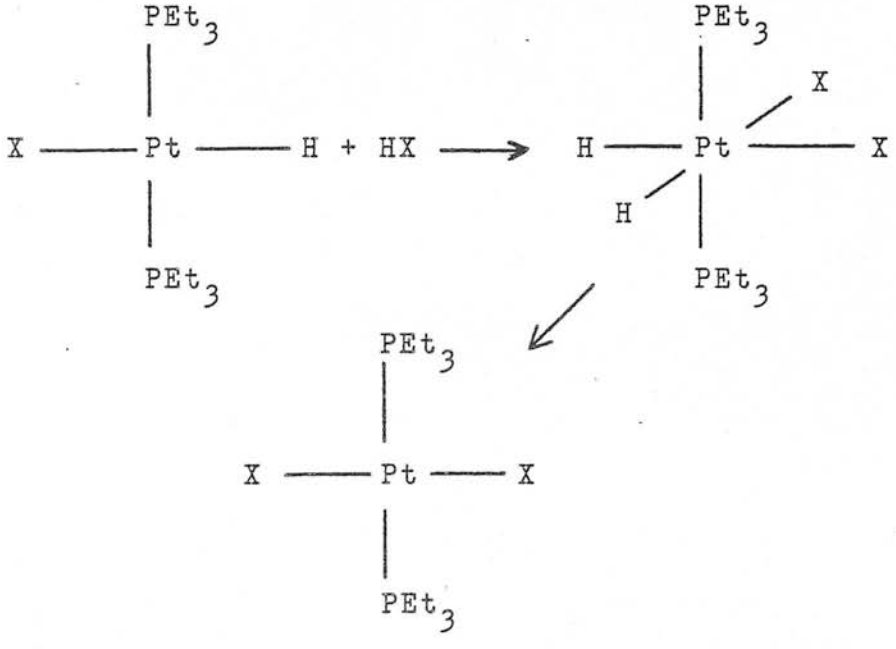
(X = Br,I,CN,NCO etc.)

Most platinum(II) complexes are square-planar and those of platinum(IV) are octahedral although other geometries are known for both of these oxidation states. The compounds used and produced in the remainder of this work generally preferred square-planar or octahedral

geometries.

One of the most widely studied classes of platinum complexes is the trans-halo-hydride phosphine complexes - $PtHX(PR_3)_2$ (X = Cl,Br,I : R = alkyl or aryl). Particularly well studied are the cases where R = Et.

Since these compounds were first prepared by Chatt and Shaw[6] in the early 60's, they have been extensively studied in this and other departments. Like most square-planar platinum(II) complexes, they undergo facile oxidative addition reactions to produce six-coordinate platinum(IV) complexes which frequently undergo reductive elimination to produce a more stable four-coordinate platinum(II) species. Early work involved the reactions with simple hydrogen halides and the six-coordinate products were isolated by the removal of solvent at low temperatures.[7] In solution at ambient temperature, these species reductively eliminated hydrogen to leave the trans-dihalo bis phosphine platinum(II) species.



Large numbers of reactions of these and related species are postulated as proceeding by an initial oxidative addition to produce an octahedral platinum(IV) species. Although modern fourier-transform n.m.r. spectrometers have simplified the task of obtaining spectra at temperatures as low as 100 K, it has still proved impossible in some reactions to detect such an intermediate before reductive elimination takes place. In many early studies, the initial products were not detected because of the limitations imposed by instruments operating in a continuous wave mode. Such instruments often only observed protons, and unless hydrides were present there was often little scope for detecting intermediate species. The metathetical reactions mentioned earlier are aided by the high trans effect[8] of the hydride ligand which tends to labilise the ligand trans to it. This effect is utilised in the reactions to substitute the trans halide with a variety of neutral ligands such as ammonia[5], diphenylphosphine[6], tertiary phosphines[10-12], tertiary amines[11], tertiary phosphites[12] and carbon monoxide[10]. The resultant cationic hydrido species can be isolated by addition of a large counter anion, typically perchlorate or tetraphenylborate:

$$PtClH(PEt_3)_2 + PEt_3 + NaClO_4 \rightarrow [PtH(PEt_3)_3]^+ClO_4^- + NaCl$$

The reaction of $PtI_2(PPh_3)_2$ with phosphine[10] results in the formation of a polymeric species containing a PH_3 group bound directly to platinum. Complexes containing coordinated PCl_3 groups have also

been prepared but by completely different routes.

$$PtCl_2 + PCl_3 \rightarrow PtCl_2(PCl_3)_2 + [PtCl_2(PCl_3)]_2 \quad 13,14.$$

$$Pt + PCl_5 \rightarrow PtCl_2(PCl_3)_2 + [PtCl_2(PCl_3)]_2 \quad 15.$$

1.2. Oxidative Addition Reactions.

Oxidative addition[16-18] is the general term used to describe a reaction in which the central atom increases both its coordination number and its oxidation state by two: it behaves as both a Lewis acid and Lewis base at the same time. The reaction may be represented as -

$$L_xM^{n+} + X\text{-}Y \rightleftharpoons L_x(X)(Y)M^{n+2}$$

This formalism involves oxidative addition in the forward direction and reductive elimination in the backward reaction.

In order that oxidative addition can occur, the central atom M must fulfill two main criteria. Firstly it must posses at least two vacant coordination sites and secondly it must posses non bonding electron density.

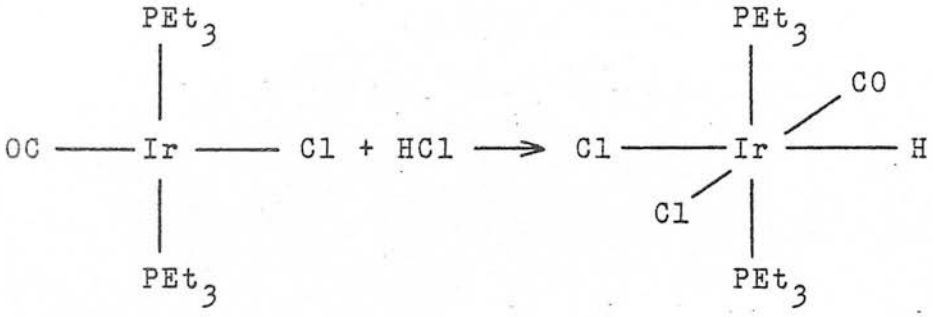
Although the majority of studies of oxidative addition reactions have been concerned with transition metal complexes, several compounds of the main group elements can also undergo this type of reaction:[18,19,21-24]

$$PF_3 + Cl_2 \rightleftharpoons PF_3Cl_2 \quad 19.$$

Probably the most widely studied of the main group elements towards oxidative addition reactions is phosphorus. Phosphorus(III) species undergo facile oxidative addition with a wide range of molecules including alcohols[25,26], ammonia[27], secondary amines[25],

hydrogen halides[25], halogens[25], peroxides[28,29] and thiols[26].

In transition metal chemistry, this type of reaction is particularly well studied in the reactions of the platinum group metals. Square planar, 16-electron d^8 complexes of these metals undergo oxidative addition to produce octahedral, 18-electron d^6 species.



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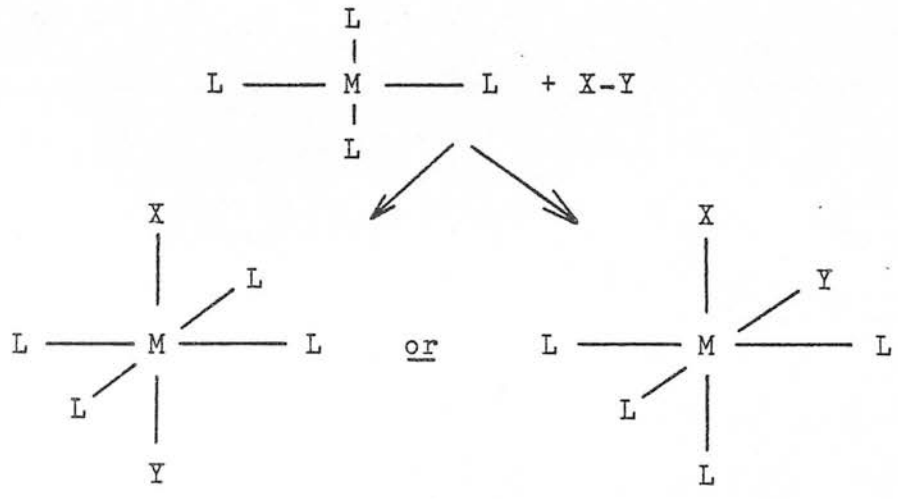
The reaction may produce cis- or trans-addition, depending on a variety of factors which are difficult to predict.

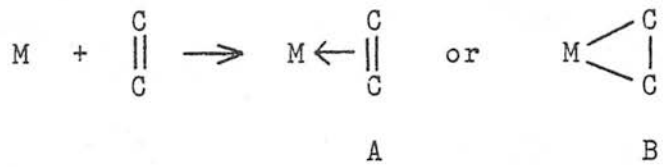


One of the main reasons for the interest in this area of chemistry is its relevance to the field of catalysis which will be discussed later in this chapter.

The position of the equilibrium between oxidative

addition and reductive elimination is complex and governed by several factors. Two of these factors tend to dominate however: firstly the energy required to raise the oxidation state of the central atom by two and secondly the energy required to cleave the X-Y bond of the molecule being added. The former of these two factors means that the equilibrium will favour oxidative addition for the heaviest element in a given group of the periodic table, assuming all other factors to be equal. It also means that the metals to the left of the table will form more stable complexes than those to the right under conditions of oxidative addition. The second factor is fairly straightforward in that a high X-Y bond energy will tend to favour reductive elimination, the bond energies M-X and M-Y must also be taken into consideration. A combination of these and other minor factors including the nature and mode of bonding of the ligands make it a complex combination of factors to rationalise why, say, platinum(II) species are more stable than platinum(IV) species but iridium(I) species are less stable than iridium(III) species.

Although the majority of reactions can be rationalised in the simple terms described, there are others which present problems. Crabtree and Hlatky[30] have pointed out that the inability to define the formal oxidation state in some cases can lead to confusion. Some so-called oxidative addition reactions are in fact not oxidative in nature. e.g.



A B

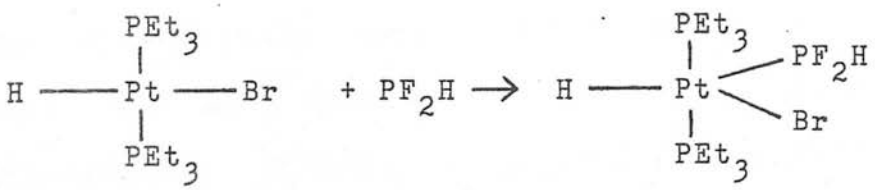
Case A is more accurately defined as a donor adduct whereas case B can be regarded as oxidative addition. The substituents present on the alkene affect which of these types of product will actually form. It has also been shown in some supposed oxidative addition reactions to iridium (I) species[31,32] that the electron density at the iridium centre actually increased upon reaction. The formal definition of oxidative addition should result in a net reduction of electron density at the metal centre upon oxidative addition:

$$[Ir(COD)_2]^+ + H_2 \longrightarrow [Ir(COD)_2H_2]^+$$

The oxidation state at the iridium centre in the above example actually changes by approximately -1 as opposed to the theoretical +2. Although the concepts and applications of oxidative addition are normally valid, care may have to be taken when dealing with non classical ligands.

1.3. Donor Adduct Formation.

Donor adduct formation, or ligand addition reactions, occurs when a ligand reacts with a complex to increase the coordination of the metal without affecting the oxidation state.



33.

A variety of trivalent phosphorus compounds form complexes with transition metals. These donor molecules are quite strong Lewis bases and give complexes with acceptors such as BR_3 compounds where d orbitals are not involved. However, the donor atoms have empty d orbitals and can act as π -acceptors. The degree of back-donation depends on the electronegativity of the substituents attached to the donor atom. Using the effect on the value of the carbonyl strching frequency in the i.r. spectrum, an order of decreasing π-acidity was obtained[34]:

$$CO \sim PF_3 > PCl_3 > PCl_2R > PClR_2 > PR_3.$$

Such correlations do not unequivably prove that PX_3 compounds have significant π-acidity. Examination of the M-PX_3 bond length showed that as the electronegativity of X was increased, greater Mdπ -> pdπ bonding, without affecting the σ-bond resulted in a shortening of the M-P bond length.[35] PF_3 is as good as or possibly better than CO[36] as a π-acceptor and it is therefore little surprise to find that large numbers of transition metal-PF_3 complexes are known. $P(CF_3)_3$ is also a strong π-acceptor but has been much less widely studied than has PF_3.

1.4. Catalysis and the platinum group metals.

It is almost beyond doubt that the reactions of the

platinum group metal complexes would not have received the enthusiastic attention of recent years had it not been for the interest caused by their catalytic properties. Wilkinson's compound,[37] $RhCl(PPH_3)_3$, acts as a hydrogenation catalyst for alkenes. The first step of this process is oxidative addition of hydrogen to the metal, cleaving the H-H bond prior to reaction with the alkene which coordinates to the rhodium at a subsequent step in the reaction. A similar activation of hydrogen is a crucial step in the catalysis of hydroformylation by $Rh(CO)H(PPh_3)_3$.[38] The activation of hydrogen by oxidative addition to neutral metal complexes was first reported by Vaska[39] and resulted in a large number of studies on the so called "Vaska's compound" - $Ir(CO)Cl(PPh_3)_2$.[40-46] The triethylphosphine analogue of Vaska's compound[47,48] was used to synthesise the first substantiated species containing a terminal $-PF_2$ group.[49] An earlier work[50] claimed to have produced such a species as a biproduct in a nickel reaction but subsequent work has cast doubts as to its validity.

1.5. Transition metal complexes containing trivalent group VB ligands.

The majority of transition metal complexes which contain a ligand based around a group VB element show four-coordination at the group VB centre. e.g. $-PR_3$, $-AsR_3$ etc. Such compounds are well known and particularly complexes containing tertiary phosphines have been the subject of numerous studies. Comparatively

few complexes have been prepared in which a three-coordinated group VB element is present. The methods by which such species have been prepared are quite varied in type.

The most widely used route involves the reaction of a group VB halide with an alkali metal salt of an anionic metal complex:

$$Ph_2BiCl + Na[Re(CO)_5] \longrightarrow Ph_2Bi\text{-}Re(CO)_5 + NaCl \quad 51.$$

$$AsCl_3 + Hg[Fe(CO)_2(NO)(PPh_3)]_2 \longrightarrow Cl_2As\text{-}Fe(CO)_2(NO)(PPh_3) \quad 52.$$

Cleavage of binuclear metal complexes with the trihalides of arsenic, antimony and bismuth has also been successfully utilised:[52,53]

$$SbCl_3 + [Fe(CO)_2Cp] \longrightarrow Cl_2Sb\text{-}Fe(CO)_2Cp$$

As an extension to this route, the reactions of diphosphines[54] and diarsines[55] with binuclear metal species also produced the desired type of product:

$$[P(CF_3)_2]_2 + [Fe(CO)_2Cp] \longrightarrow 2\ (F_3C)_2P\text{-}Fe(CO)_2Cp$$

Deprotonation of secondary phosphines coordinated to a variety of transition metal species using alkyl lithiums has also met with limited success:[56]

$$W(CO)_5(PPh_2H) + BuLi \longrightarrow [Ph_2P\text{-}W(CO)_5]^- + BuH$$

From 1973 onwards, the group led by Malisch at Wurtzburg has dominated this area of chemistry by reacting group VB halo-species with a wide variety of transition metal anions of the general type - $[M(CO)_nCp]^-$. [57-66] Reaction of phosphorus trichloride with a group VIA metal silyl complex generated a product containing a terminal $-PCl_2$ group:[63]

$$(Me_3Si)M(CO)_3Cp + PCl_3 \longrightarrow Cl_2P\text{-}M(CO)_2Cp + Me_3SiCl$$

M = Cr, Mo or W.

Reaction of $IrCl(CO)(PEt_3)_2$ with PCl_3[49] or ClF_2P[66] produced thermally stable six-coordinate iridium(III) species containing terminal $-PCl_2$ and $-PF_2$ groups respectively.

1.6. Reactivity of complexes containing three-coordinate group VB ligands.

Once species of this types were synthesised, the potential for reaction at the group VB centre was quickly exploited. They often react as do standard trivalent group VB ligands.[56,60,68-71] Studies have involved quaternerisation,[72,73] protonation,[70] reaction with halogens[74] and reactions with group VIB elements.[33,73,76] Reactions to produce bridges to boron[33,76,77] and to other transition metal species[77] have also been the subject of recent interest.

Collectively, these reactions tend to suggest that the group VB centre is nucleophilic in character. The facile addition of group VIB elements to this centre can be rationalised on the basis of high electron density resulting in the ease of oxidation to relieve what is essentially an unfavourable electronic environment.

1.7. Hydrides of phosphorus in higher coordination than 3.

Although phosphorus compounds in 4, 5 and 6-coorination are well known, the number of examples containing phosphorus-hydrogen bonds is remarkably small. The most common examples are the oxo-acids. Both hypophosphorus and phosphorus acids fit into this category.

Hypophosphorus acid is a powerful reducing agent which readily disproportionates to the more stable phosphorus acid and phosphine. These species all contain four-coordinated phosphorus. Compounds containing hydrogen bound to five-coordinate phosphorus are much less well known.

PH_5 itself does not exist; PH_4I has been prepared and characterised[78] and of course contains tetrahedral $[PH_4]^+$. PHF_4 and PH_2F_3 have been prepared in low yield by the reaction of HF with phosphorus acid and hypophosphorus acids respectively[79,80] or in higher yield by the gas-phase reaction of PF_3 with trimethylsilane.[80] To date, there have been no substantiated reports of any similar species containing either chloride or bromide. The reaction of PF_4H or PF_2H_2 with base produces the anions $[PHF_5]^-$ and $[PH_2F_4]^-$ respectively,[80] the only hydride derivative of six-coordinate phosphorus.

1.8. Nuclear magnetic resonance (N.m.r.) spectroscopy.

The principal investigative tool used in the course of this work was n.m.r. spectroscopy. There are numerous comprehensive texts on this subject and it is unnecessary for this work to discuss the basic principles. However, it is worth considering some of the more specialised aspects which are of direct relevance to this work.

Almost all of the compounds studied contained tertiary alkyl phosphines coordinated to either platinum or iridium metal centres. Iridium has two isotopes, ^{191}Ir, 37.3% - I = $^{3}/2$ and ^{193}Ir, 62.7% - I = $^{3}/2$. The quadropolar moment of both of these nuclei is very high. It has not proven possible to directly observe either isotope due partly to quadropolar broadening and also to the very low frequency at which they resonate (1.718 & 1.871 MHz respectively on the scale at which protons resonate at 100 MHz.). No coupling or detectable broadening has been observed between iridium and another spinning nucleus to which it is directly bound. This is attributed to the very rapid rate of relaxation of the iridium nucleus resulting in effective self-decoupling from the other nucleus.

Platinum on the other hand posseses six isotopes of which only ^{195}Pt (33.7%) posseses a spin - I = $^{1}/2$. For a transition metal, platinum resonates at a high frequency - 12.212 MHz on the scale at which protons resonate at 100 MHz. It is nineteen times as sensitive as ^{13}C and can be directly observed given the requisite hardware. Although the chemical shift range for platinum

is very large (see Appendix), it relaxes sufficiently quickly that high speed pulsing is possible. Typically, a $^{195}Pt-\{^{1}H\}$ n.m.r. spectrum on 0.1 mM of sample can be obtained after about one hour of accumulation. When platinum couples to another spinning nucleus, the spectrum of the other nucleus shows so-called platinum satellites to either side of the main resonance. The intensity pattern of 1:4:1 arises from the 33.7% abundance of spinning platinum present. In cases where the complex being studied contains a tertiary phosphine and/or a hydride, a great deal of information can be obtained from both the chemical shifts and coupling constants in the phosphorus and proton n.m.r. spectra.

Transition metal hydrides are almost invariably found to resonate at less than 0 p.p.m. The large chemical shifts of hydrides are attributed to the non bonding electrons of the metal shielding the proton.[82] In platinum(II) complexes; this shielding arises from the 5d electrons.[83] The large shifts of hydrides mean that there is little chance of hydride resonances being obscured by other more intense resonances from alkyl protons etc. The coupling between platinum and hydrides is very dependant on the nature of the ligand trans to the hydride. This variation is largely determined by the Fermi contact interaction[84] which is dependant on three major factors: the degree of s character in the platinum-hydrogen bond, the degree of s character at each nucleus and the mean excitation energy. The final term is itself dependant on the ligand field splitting

parameter. It is found that this term dominates as long as the trans ligands are sufficiently different to give reasonable differences in the mean excitation energy. If this is not the case, then the degree of s character in the platinum-hydrogen bond tends to dominate and determines the magnitude of the coupling constant.

Large amounts of data have been collected regarding phosphorus chemical shifts[85,86] but the interpretation is by no means simple. The major terms which contribute to the chemical shift have long been known[87] but the complexities involved in prediction are formidable. The chemical shift of a tertiary phosphine always moves to higher frequency on coordination to a transition metal reflecting the reduction in shielding caused by the metal orbitals.[88]

The value of the platinum-phosphorus coupling constant is dependant on the coordination number at platinum and on the nature of the ligand trans to the phosphorus as described for hydrides. The coupling constant for a six-coordinate platinum(IV) species is usually less than 1800 Hz.[89] The value for a four-coordinate platinum(II) species is normally in the range 2000 $\rightarrow$ 7000 Hz. This can be rationalised on the basis of the different amounts of s character in the the platinum-phosphorus bond for the two geometries. Octahedral coordination may be regarded as d^2sp^3 hybridised and square planar as being dsp^2. The higher percentage of s character in the latter geometry results in the significantly larger value of the

platinum-phosphorus coupling constant.

The trend in phosphorus-hydrogen couplings in phosphines and phosphoranes is quite the reverse. The higher the the coordination number at phosphorus, the larger is the coupling constant. $-PH_2^-$ shows a phosphorus-hydrogen coupling of 130 Hz. Three-coordinate phosphorus species generally fall in the range 180 → 230 Hz. Four-coordination at phosphorus results in the range increasing to 250 → 700 Hz and those associated with five-coordinate phosphorus are in the range 700 → 950 Hz. The variation in coupling constant with coordination number is once again a consequence of the degree of s character in the bond. PH_3 is pyramidal with an HPH angle of 93.7° reflecting a very low s character in the hybrid orbitals. Increasing the coordination number results in the HPH angle opening up and the s component increasing thus increasing the size of the phosphorus-hydrogen coupling constant.

Phosphorus-hydrogen coupling constants are also noted to increase with the attachment at phosphorus of electronegative groups. This reflects a change in the local hybridisation involving the phosphorus-hydrogen bond,[90] and in HPF_4 leads to the exceptional case where the phosphorus-hydrogen coupling constant of 1090 Hz,[91] is greater than the phosphorus-fluorine coupling contant of 892 Hz. It should also be noted that phosphorus-fluorine couplings decrease with increasing coordination number at phosphorus.

Limited use will be made in this work of n.m.r.

pulse sequences. Due to the complexities of the theory governing this topic, no explanation will be given but reference should be made to the review by Gunther.[92]

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CHAPTER 2.

EXPERIMENTAL TECHNIQUES and PREPARATIONS.

2.1 Experimental Techniques.

2.1.1 Apparatus for Preparation.

Throughout the course of this work, two different types of handling systems were utilised. A conventional design of high vacuum system was used to manipulate and measure volatile reagents. The sealing of n.m.r. tubes was always carried out on this line. A Schlenk type line was used to facilitate the handling of air or moisture sensitive compounds which were either too involatile to be handled on the high vacuum system or which interfered with the grease on this line.

The high vacuum line was consructed in Pyrex glass and the high vacuum ($\sim 10^{-5}$ τ.) was obtained by a glass, three-stage mercury diffusion pump backed by a rotary oil pump that provided a roughing vacuum of ca. 10^{-2} τ. The degree of vacuum was monitored by a Pirani-type gauge. Pressures of volatile reagents within the line were measured by a spiral gauge with mirror operating as a null zero device with lamp and scale. The line was made up of detachable sections joined by ground glass joints to facilitate cleaning. Apiezon L and N greases were used on the ground glass joints and stopcocks respectively. N.m.r. tubes were of conventional 5 m.m. design and attached to the vacuum line via a B10 ground glass joint. Reaction ampules were all fitted with "Soveril" greaseless taps and attached to the vacuum line via a ground glass joint. The volumes of the individual

sections of the vacuum line were obtained using a molecular weight bulb of known volume, enabling rapid quantitative measurements of volatile reagents.

The Schlenk line is, in essence, a combined vacuum-nitrogen line. Utilising a manifold fitted with a series of three-way taps, either vacuum or nitrogen is available at the end of rubber pressure tubing attached to each of the three-way taps. Vacuum was supplied from a rotary oil pump via a trap held at 77 K. Commercial "White Spot" nitrogen was dried and deoxygenated by passing through 1.5 m. columns containing Phosphorus Pentoxide and BASF catalyst R3-11 respectively. Using standard design B24 Schlenk tubes it was possible to manipulate all but the most sensitive of compounds in a quick and convenient manner.

2.1.2. Criteria of purity.

The purity of reagents was checked by various methods. For volatile reagents, infra-red spectroscopy was the main tool used to check for impurities. Such impurities were generally removed by trap to trap distillation through traps held at reduced temperatures by "slush baths" of standard temperatures. (table 2.1)

^{31}P and ^{1}H n.m.r. spectroscopy and C and H elemental analysis were used to establish the purity of the metal substrates.

TABLE 2.1 STANDARD SLUSH BATH TEMPERATURES.

SOLVENT	TEMPERATURE	
	^{o}K	^{o}C
Carbon Tetrachloride	249	-24
Arklone	240	-33
Chlorobenzene	227	-46
Chloroform	210	-63
Acetone	195	-78
Toluene	177	-96
Carbon Disulphide	161	-112
Diethyl Ether	153	-120
n-Pentane	143	-130
40-60 Pet Ether	128	-145
iso-Pentane	113	-160

All baths were produced by slushing the desired solvent with liquid nitrogen except in the case of acetone which is merely used as a support for solid carbon dioxide.

2.1.3. Instrumentation.

Infra-red spectra were recorded on a Perkin Elmer PE 598 double beam grating spectrometer (range 200-4000 cm^{-1}). Gas phase spectra were obtained using a glass gas cell with a path length of 10 cm. fitted with KBr end windows attached with Apiezon W cement. The cell was

attached to the line via a ground glass joint. Mull spectra of solids were recorded using CsI plates with nujol or hexachlorobutadiene (dried over molecular seive) used as mulling agent.

Nuclear magnetic resonance (N.m.r.) spectra were recorded on a variety of instruments as detailed below. Chemical shifts were measured in p.p.m. as positive to high frequency of the following standards :-
^{11}B - $BF_3(OEt_2)$, ^{19}F - CCl_3F, ^{1}H - Me_4Si, ^{31}P - 85% H_3PO_4, ^{195}Pt - $(PtCl_4)^-$ and ^{77}Se - Me_2Se.

JEOL FX60Q : Fourier Transform ^{31}P spectrometer operating at 24.21 MHz. fitted with variable temperature facility. Broad band and selective proton decoupling facilities available.

BRUKER WP80SY : Fourier Transform ^{1}H and ^{19}F spectrometer operating at 80.13 and 75.39 MHz respectively and fitted with variable temperature facility. Homonuclear proton decoupling and both broad band and selective heteronuclear proton decoupling facilities were available.

BRUKER WP200SY : Fourier Transform multinuclear spectrometer with variable temperature facility was used to observe ^{1}H (200.13 MHz), ^{11}B (64.21 MHz), ^{77}Se (38.168 MHz), ^{31}P (81.02 MHz), and ^{195}Pt (42.83 MHz). Full homonuclear proton decoupling facilities were available but only broad

band proton decoupling was possible whilst observing other nuclei.

BRUKER WH360 : Fourier Transform multinuclear high field spectrometer with variable temperature facility was used to observe ^{1}H (360.13 MHz), ^{31}P (145.78 MHz) and ^{77}Se (68.546 MHz). Both broad band and selective proton decoupling, and selective homonuclear phosphorus decoupling facilities were available.

2.2 Preparation of volatile reagents.

Procedures for the preparation and purification of the volatile reagents used during the course of this work are detailed below. Appropriate references and any modifications to the standard techniques are detailed. Purity checks were applied to commercial starting materials as appropriate.

2.2.1. Boron Trichloride : commercial boron trichloride contains large amounts of HCl which is removed by repeated fractionation through a 195K bath. Although large amounts pass this bath, the retained fraction is spectroscopically free of HCl.

2.2.2. Diborane[1] : prepared by the reaction of potassium borohydride with ortho - phosphoric acid.

2.2.3. Fluorotrimethylgermane[2] : prepared by the overnight reaction of chlorotrimethylgermane with

a ten - fold excess of freshly prepared lead (II) fluoride. 100% conversion is obtained if the lead (II) fluoride is dry and fresh.

2.2.4. Trimethylstannane[3] : a sample, prepared by the reduction of chlorotrimethylstannane with lithium tetrahydidoaluminate, was kindly donated by Mr. R. A. Mayo.

2.2.5. Bromo difluorophosphine[4] : prepared by the reaction of anhydrous HBr with difluorophosphine dimethylamide.

2.2.6. Chloro difluorophosphine[4] : prepared by the reaction of anhydrous HCl with a slight excess of difluorophosphine dimethylamide

2.2.7. Iodo difluorophosphine[4] : prepared by the reaction of anhydrous HI with a slight deficit of difluorophosphine dimethylamide

2.2.8. Hydrogen Bromide[5] : prepared by the reaction of elemental bromine with tetrahydronaphthalene and purified by fractionation through a 153 K bath.

2.2.9. Hydrogen Chloride[6] : prepared by the dehydration of concentrated hydrochloric acid with an excess of concentrated sulphuric acid.

2.2.10. Hydrogen Iodide[7] : prepared by the dehydration of hydroiodic acid with an excess of phosphorus pentoxide.

2.2.11. Hydrogen Sulphide[8] : prepared by the reaction of iron (II) sulphide with 2 molar sulphuric acid and purified by fractionation through a 177 K bath.

2.2.12. Hydrogen Selenide[8] : prepared by the reaction of

freshly prepared aluminium selenide with 2 molar sulphuric acid and purified by fractionation through a 177 K bath.

2.2.12. Dinitrogen Tetroxide[9] : prepared by the thermal decomposition of lead (II) nitrate and purified by fractionation through a 195 K bath.

2.2.13. Phosphorus Pentafluoride[10] :prepared by the thermal decomposition of commercial Phosfluorogen A under reduced pressure and purified by fractionation through a 153 K bath.

2.2.14. Dichlorodimethylamminophosphine[11] : prepared by the reaction between phosphorus trichloride and dimethylammine in the absence of solvent. The resultant mixture was distilled at atmospheric pressure under nitrogen. The product distilled at 320 K.

Commercial samples of anhydrous methylammine and trimethylammine were dried overnight in glass ampules over powdered potassium hydroxide prior to use. Commercial phosphorus trichloride was fractionated through a 195 K bath and that which stopped was stored in a glass ampule containing roasted molecular seive 4A to remove any remaining HCl. Commercial Phosphorus tribromide was purified by blowing dry oxygen-free nitrogen through it prior to freeze degassing on a vaccum line. Chlorine was obtained from a commercial cylinder and was purified by repeated fractionation through baths held at 153 K and 195

K to remove HCl and water respectively. The sample of xenon difluoride[11] was kindly prepared and donated by Dr. R.W. Cockman. Commercial ammonia was purified by distillation off sodium wire. Carbon monoxide (Technical grade) was used as supplied. Phosphorus pentachloride was used as supplied but handled under a nitrogen atmosphere to prevent hydrolysis.

2.3. Solvents

The various solvents used were purified as follows :

Dichloromethane - commercial grade, dried over roasted molecular seive

Acetone - commercial grade, dried over roasted molecular seive

Toluene - commercial grade, dried over potassium

Di ethyl ether - commercial grade, dried over sodium wire

n-Pentane - commercial grade, dried over sodium wire

Triethyl phosphine - commercial grade, used as supplied

2-Dichlorobenzene - commercial grade, used as supplied.

Ethanol - 250 ml. of commercial ethanol was refluxed under nitrogen in the presence of 5g magnesium turnings for ca. 30 minutes. Dry ethanol was then distilled off and stored over

molecular seive under nitrogen.

Methanol - 250 ml. of commercial methanol was refluxed under nitrogen in the presence of 5g magnesium turnings for ca. 30 minutes. Dry methanol was then distilled off and stored over molecular seive under nitrogen.

Deuterated n.m.r. solvents were dried as appropriate and distilled prior to use.

2.4. Preparation of standard metal substrates.

2.4.1. $IrCl(CO)(PEt_3)_2$ [12] : the compound $[\{Ir(C_8H_{14})\}_2Cl]_2$ was prepared from commercial $IrCl_3$ by literature methods.[13] 0.45 g of this material was stirred in a Schlenk tube ,under nitrogen, in dry degassed acetone for 15 minutes. Carbon monoxide was then gently bubbled into the solution until the orange colour was replaced by an intense deep blue colour. (5 minutes) Triethyl phosphine (0.3 ml. in 5ml. dry degassed acetone) was then added dropwise to the blue solution and the mixture stirred for 1 hour under nitrogen. The resulting yellow solution was filtered under nitrogen and the solvent removed under vacuum. The residual oil was heated to 80°C for 4 hours under vacuum to remove the displaced cyclooctene. The resulting solid was sublimed at 120° C to yield yellow crystals of the product. Although air sensitive, these can be handled in air for brief periods of time.

$IrBr(CO)(PEt_3)_2$: prepared by halogen metathesis of the standard chloro species described above using an excess of lithium bromide in acetone. The solvent was removed under vacuum and the product sublimed from the reaction mixture at 125° C. under high vacuum.

2.4.2. $\underline{cis\text{-}PtCl_2(PEt_3)_2}$ [14] : prepared by the direct reaction of triethylphosphine with platinum dichloride in acetone. (A small amount of the trans isomer formed but is readily removed by washing with diethylether.) Recrystalisation from dichloromethane yielded a white solid.

2.4.3. $\underline{Trans}$ - $\underline{PtClH(PEt_3)_2}$ [15] : prepared by the reduction of an aqueous suspension the cis-dichloro species with an excess of Hydrazine Hydrate at 100° C. The oil was allowed to cool and solidify before being recrystallised from dichloromethane to yield white crystals.

2.4.4. $\underline{Trans}$ - $\underline{PtHX(PEt_3)_2}$ (X = Br or I) : prepared by halogen metathesis of the standard chloro compound using LiBr or NaI as appropriate in acetone. The solutions were reduced to dryness and the desired product extracted with dichloromethane.

2.4.5. $\underline{[PtH(PEt_3)_3]^+BPh_4^-}$ [16] : prepared by stirring trans - $PtClH(PEt_3)_2$ with $NaBPh_4$ and triethylphosphine in methanol. The product so precipitated requires no further purification.

2.4.6. $\underline{Trans}$ - $\underline{PtClH(PCy_3)_2}$ [17] : prepared by phosphine exchange between the corresponding triethyl species and tricyclohexylphosphine in toluene solution at reflux for

six hours. Solvent and liberated triethylphosphine were then distilled off and the solid residue washed with hexane and methanol prior to recrystalisation from dichloromethane.

2.4.7. trans - $PtH_2(PCy_3)_2$[18] : a refluxing ethanolic solution of trans - $PtClH(PCy_3)_2$ was treated with an excess of a filtered solution of $NaBH_4$ in ethanol under N_2. After two hours the crude product was filtered off, washed with methanol and recrystallised from dichloromethane.

2.4.8. $Pt_2Cl_4(PEt_3)_2$[19] : prepared by stirring a slurry of an equimolar mixture of the cis- $PtCl_2(PEt_3)_2$ and $PtCl_2$ in 2-dichlorobenzene at its boiling point under nitrogen. Crude product was precipitated with diethyl ether, filtered off and recrystalised from dichloromethane.

2.4.9. $RhCl(CO)(PEt_3)_2$[20] :was prepared by reacting 1.57 g. $RhCl_3$ dissolved in 30 ml. of a 1:1 mixture of ethanol and methanol with 1.8 ml triethyl phosphine under nitrogen. 18 ml. molar potassium hydroxide was then added and the mixture refluxed under nitrogen for 1 hour. The mixture was cooled in ice and the resulting precipitate removed by filtration. The solid was dried under vacuum then sublimed at 110° C. to yield yellow air sensitive crystals.

$Ph_3C^+BF_4^-$ was prepared by the reaction of propionic anhydride with triphenyl methanol at 373 K. The resulting mixture was cooled to ambient temperature and 48 % fluoroboric acid added. Cooling in an ice bath

precipitated out the white product which was filtered off and dried on a vacuum line prior to use

Samples of $[RhCl_2(C_5Me_5)]_2$[21] and $[RuCl_2(p\text{-cymene})]_2$[22] were prepared by the standard literature methods and kindly donated by Mr. J.D.Fotheringham. $[W(C_5H_5)(CO)_3]_2$[23] was prepared by the standard literature method and kindly donated by Mr. A.McIntosh.

2.5. Preparation of t - $PtCl(PCl_2)(PEt_3)_2$

This species was prepared as required by the reaction of a solution of trans - $PtClH(PEt_3)_2$ in d^2 dichloromethane with phosphorus trichloride in the presence of an equimolar amount of trimethylamine. The mixture was allowed to warm to room temperature for 5 minutes before being cooled to 177 K. At this temperature, the trimethylammonium chloride by-product is virtually insoluble and was removed by filtration into a n.m.r. tube (fitted with a B10 cone) using a Schlenk line. The solution was then cooled to 77 K and the other reagent condensed in and the n.m.r. tube sealed as normal. In the case where the second reagent was a solid, the n.m.r. tube was held at 77 K under a nitrogen atmosphere and the other reagent added under a flow of nitrogen. The n.m.r. tube was then fiitted to the vacuum line, (still at 77 K) evacuated and sealed as normal.

2.6. Attempted isolation of t - $PtCl(PCl_2)(PEt_3)_2$

Initial attempts to isolate the title compound involved following the synthesis detailed in the previous section but filtering at 77 K into a Schlenk tube rather than an n.m.r. tube. The solvent (CH_2Cl_2 in this case) was then pumped off to leave an orange oil. Despite a large number of attempts to produce a solid sample from this oil, none was succesful. ^1H n.m.r. spectroscopy showed the presence of small amounts of the trimethylammoniun chloride (ca. 5%) by-product to be present. It was not possible to completely remove this impurity from the sample by conventional means and it was thought possible that this prevented solid formation. It is also possible, though less likely, that the title compound is actually an oil in its natural state. If it was the presence of the trimethylammonium salt which was preventing solid formation, and this could not be completely removed, the alternative was to produce the title compound by a route which did not form this impurity. The reaction described in Chapter 3 between phosphrus trichloride and $[PtH(PEt_3)_3]^+$ was shown to produce large amounts of the title compound contaminated with only a little (10%) of the starting cation at temperatures of up to ca. 240 K. When a sample of this mixture was prepared, it proved impossible to separate the components by conventional methods. Attempts to separate this mixture using low temperature chromatography under an inert atmosphere failed despite

trying a wide range of stationary phases and solvents. Attempting to remove the excess cation by essentially titrating with phosphorus trichloride resulted in the production of decomposition products rather than the desired result.

2.7. Preparation and utilisation of a standard solution of PBr_3 in CD_2Cl_2

The reactions detailed in Chapter 3 present little problem in accurate measurement of the phosphorus trichloride as it is sufficiently volatile to enable standard vacuum line techniques to be employed. Phosphorus tribromide however has a significantly lower vapour pressure at ambient temperature (ca.3mm) and dissolves rapidly in the greases employed in the vacuum line. Various attempts were made to measure phosphorus tribromide using the equilibrium vapour pressure in a large volume, but none proved to be sufficiently accurate for the purposes of this work. As all the reactions in Chapter 3 which used phosphorus tribromide used CD_2Cl_2 as the n.m.r. solvent, it was decided to prepare a standard solution such that the volume of solvent required for the n.m.r. experiment would contain 0.1 mM of phosphorus tribromide. Slight discrepancies could be compensated for by adjusting the amount of platinum substrate used to fit the exact concentration of the standard solution.

A sample of phosphorus tribromide was purified as described in Chapter 2.2. Working in a glove bag, under an atmosphere of nitrogen, 1.9 ml. of phosphorus

tribromide was syringed into 10 ml CD_2Cl_2. The mixture was then transferred to the calibrated vessel shown in fig.2.1. Two 0.4 ml aliquotes were then removed and hydrolysed excess sodium carbonate solution. The organic layer was separated and rejected. The aqueous layers were then treated with dilute nitric acid and excess silver nitrate solution added. The solutions were boiled for a short time before cooling to room temperature and the precipitated silver bromide filtered off into preweighed Gooch funnels. The samples were dried and weighed and the bromide content calculated.

In a typical experiment, the required platinum substrate was weighed into an n.m.r. tube fitted with a B10 cone and connected to the calibrated vessel. The tube was evacuated and cooled to 77 K. Pumping was ceased and 0.4 ml. of standard solution added. The solution froze almost immediately and little reaction occured at this stage. The n.m.r. tube was then sealed and stored at 77 K until required for the n.m.r. study.

2.8. Experiments Involving the Reactions of

$PtCl(PEt_3)_2(PH_2X_2)$ (X = Cl or Br)

The above mentioned reactions rely on the preformation of the (PH_2X_2) species. Particularly in the case where X = Cl, the preformation reaction was not always consistent and it was deemed necessary to check that the (PH_2X_2) species had indeed formed in sufficient concentration before continuing with addition of the second reagent. The only way to monitor the concentration of the (PH_2X_2) species was by ^{31}P n.m.r. at

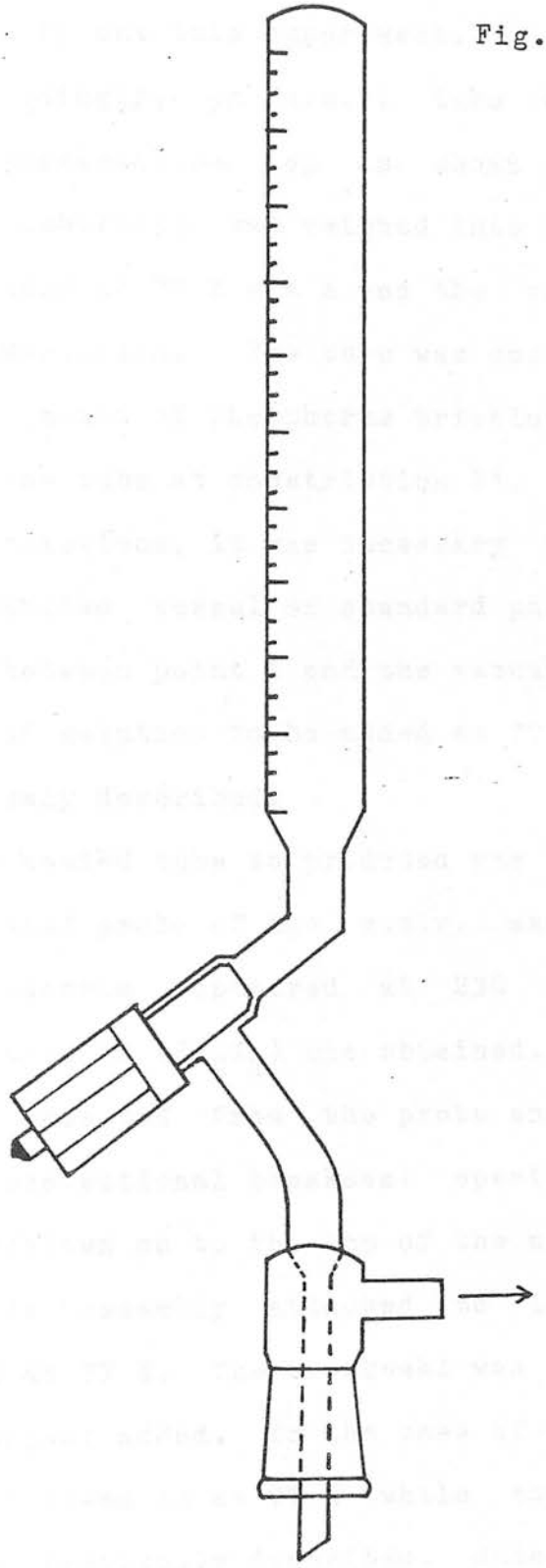

Fig.2.1. Calibrated dispenser for PBr_3 sloution.

reduced temperatures, necessitating the use of a sealed tube to carry out this experiment.

Accordingly, an n.m.r. tube was built with an integral breakseal on top as shown in fig.2.2. The platinum substrate was weighed into the tube and CD_2Cl_2 solvent added at 77 K via A and the contents warmed to allow dissolution. The tube was cooled to 77 K and the requisite amount of phosphorus trichloride added before sealing the tube at constriction S1. In the case of the (PH_2Br_2) reactions, it was necessary to have connected the calibrated vessel of standard phosphorus tribromide solution between point A and the vacuum line to enable 0.4 ml of solution to be added at 77 K prior to sealing as previously described.

The sealed tube so produced was then transferred to the precooled probe of the n.m.r. machine and the ^{31}P n.m.r. spectrum monitored at 230 K until the desired concentration of (PH_2X_2) was obtained. The n.m.r. tube was then removed from the probe and rapidly cooled to 77 K. A conventional breakseal opening attachment was then glassblown on to the top of the n.m.r. breakseal and the entire assembly attached to the vacuum line and evacuated at 77 K. The breakseal was then opened and the second reagent added. In the case of a volatile reagent, it was condensed in at 77 K while solid reagents were added as previously described. Once the second reagent had been added, the tube was then sealed at constriction S2 and the tube stored at 77 K until required.

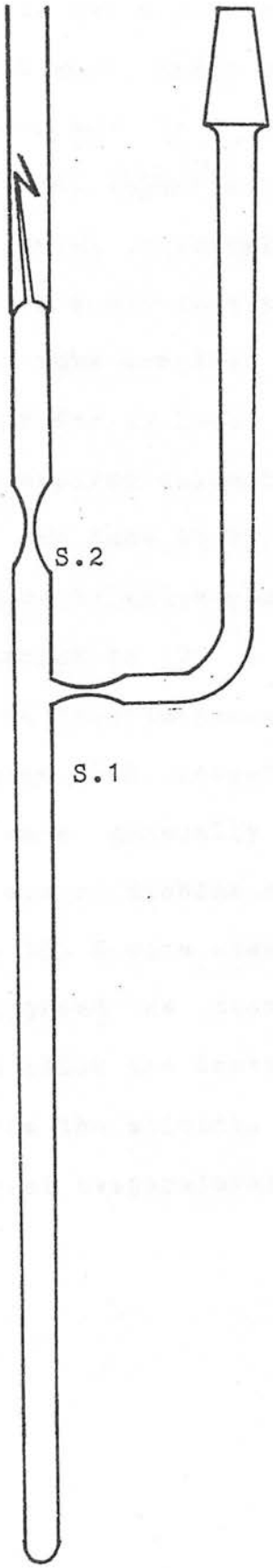

FIG.2.2

N.m.r. tube with integral breakseal.

2.9. The Conventional N.m.r. Experiment

In the majority of the n.m.r. experiments carried out in the course of this work, there was no need for the complex procedures described in the previous two sections. The conventional experiment involved weighing 0.1 mM of the required metal substrate into a 5 mm. n.m.r. tube fitted with a B10 cone and constriction to facilitate sealing. The tube was then attached to the vacuum line and pumped on for at least one hour to ensure complete dryness. The desired solvent, normally CD_2Cl_2, was then distilled into the tube at 77 K and allowed to warm to room temperature to allow complete dissolution. The sample was then recooled to 77 K and the desired reagent condensed in at this temperature. The tube was sealed at the constriction and stored at 77 K until required. Samples were generally placed into the precooled probe of the n.m.r. machine at 178 K although temperatures as low as 153 K were used on occasion. The n.m.r. spectrum was recorded as soon as the solvent melted sufficiently to allow the instrument to lock onto the Deuterium signal from the solvent. Further spectra were recorded at different temperatures as required.

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CHAPTER 3

REACTIONS OF $PtHY(PEt_3)_2$ WITH PX_3

(X = Cl or Br : Y = Cl, Br or I)

3.1. Introduction.

Recent work[1,2] in this department has resulted in the synthesis of six-coordinate iridium(III) species containing terminal $-PCl_2$ and $-PF_2$ groups. These compounds are novel in that they may be regarded as tertiary phosphines in which one of the ligands is exceptionally large and posseses unusual electronic character. The reactions which these compounds undergo are both wide-ranging and varied in type. The species containing the terminal $-PF_2$ group has been used to produce PF_2 bridges to other transition metal centres. Whereas mixed-metal bridged species are not particularly novel, the presence of a bridging PF_2 group imparts a degree of interest to these species. Both the $-PCl_2$ and the $-PF_2$ species undergo reaction at the unique phosphorus centre to produce a variety of complexes containing unusual ligands such as $-PH_2Se$.[2]

One constraint placed upon the chemistry of both of these species is that the iridium centre is effectively coordinatively saturated. For this reason, the preparation of a four-coordinate platinum(II) species containing either a terminal $-PCl_2$ or $-PF_2$ group is highly desirable. In addition to the same potential range of reactions as the iridium species, the platinum centre provides an alternative reaction centre. Previous attempts to generate a terminal PF_2 species by the reaction of PF_2Cl with $PtClH(PEt_3)_2$ resulted in the formation of the binuclear species $PtCl(PEt_3)_2(PF_2)PtCl(PEt_3)_2$[3] which contains a $-PF_2$

bridge.

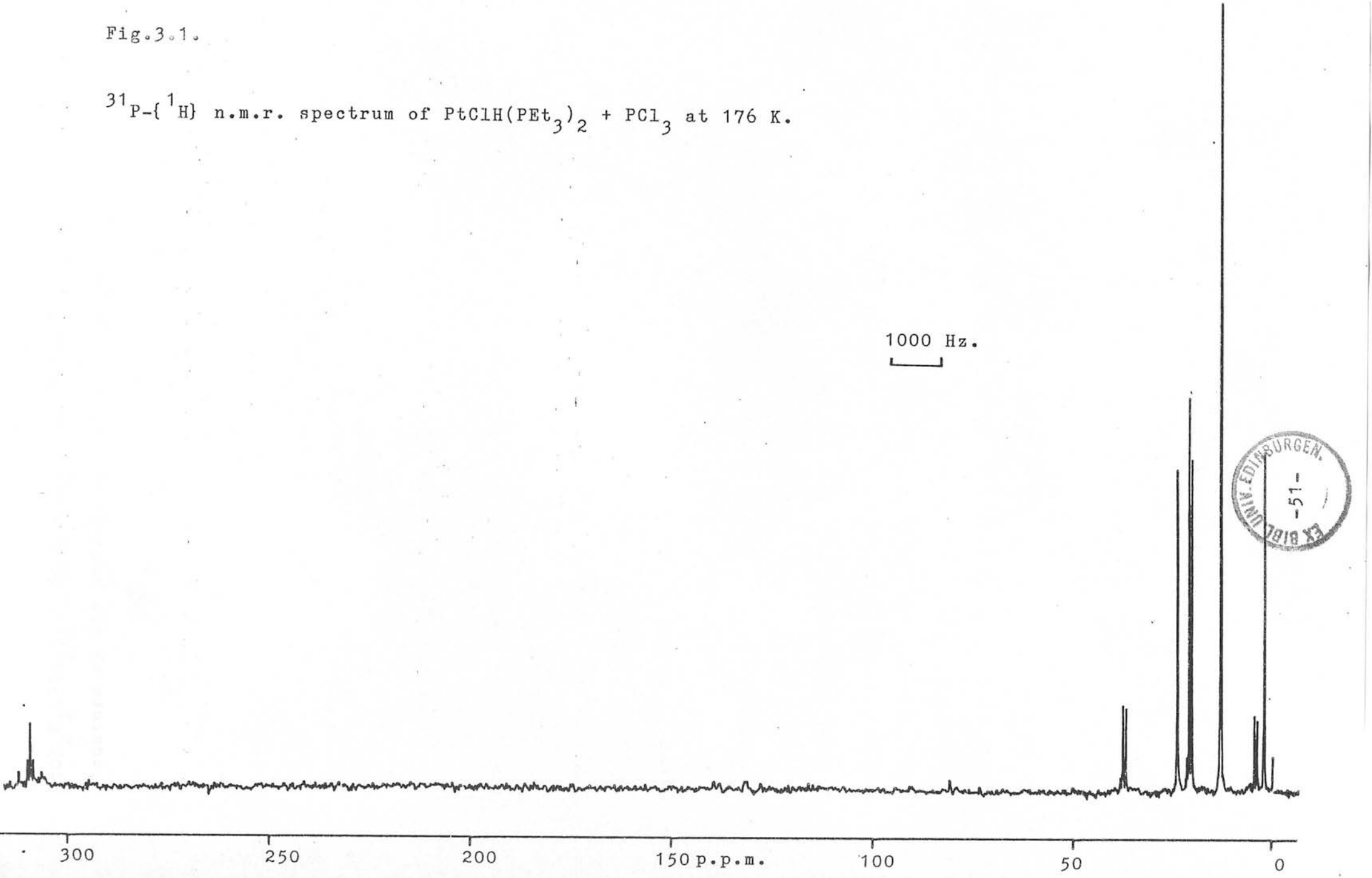
It was therefore decided to attempt the synthesis of species containing a terminal $-PCl_2$ group by the reaction of $PtHX(PEt_3)_2$ with PCl_3 or PBr_3. No reactions were undertaken utilising PI_3 due to its virtual insolubility in all common solvents conducive to n.m.r. spectroscopy.

3.2. Reactions of $PtClH(PEt_3)_2$ with PCl_3.

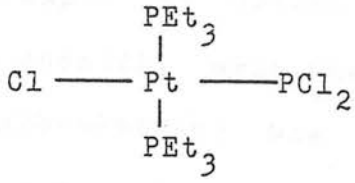
The initial reaction studied contained stoicheiometric amounts of the two reagents. Reaction was rapid and as soon as the solvent melted the $^{31}P-\{^1H\}$ n.m.r. spectrum (fig.3.1) showed, in addition to resonances associated with the two starting materials, a singlet with platinum satellites which was identified by its parameters as $PtCl_2H_2(PEt_3)_2$.[4] Additionally, a narrow doublet with platinum satellites was centered at +20.4 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. A narrow triplet, also with platinum satellites, was centered at +311.1 p.p.m. and had a coupling corresponding to that in the doublet resonance. The chemical shift of the triplet is in a region normally associated with transition metal $-PCl_2$ groups.[2,5] Retention of proton coupling broadened the triethylphosphine resonance but had no effect on the high frequency signal. The ^1H nmr spectrum of the low frequency region showed only one hydride, attributed to

Fig.3.1.

$^{31}P-\{^{1}H\}$ n.m.r. spectrum of $PtClH(PEt_3)_2 + PCl_3$ at 176 K.



$PtCl_2H_2(PEt_3)_2$. On the basis of these observations, the structure of the product was assigned as being :-



$\delta P = +20.4$ p.p.m. $\quad \delta P' = +311.1$ p.p.m.

$^1J_{PtP} = 2638$ Hz. $\quad ^1J_{PtP'} = 465$ Hz.

$^2J_{PP'} = 59$ Hz.

All parameters were recorded in dichlomethane at 180 K.

The formation of this species can be rationalised by an initial oxidative addition of PCl_3 across the platinum centre, giving rise to the six-coordinate platinum(IV) species $PtHCl_2(PEt_3)_2(P'Cl_2)$. Rapid reductive elimination of HCl from this species gives the observed product. The eliminated HCl then oxidatively adds to some, as yet unreacted, $PtClH(PEt_3)_2$, thus accounting for the formation of an equimolar amount of $PtCl_2H_2(PEt_3)_2$. To test this hypothesis, the reaction between $PtClH(PEt_3)_2$ was carried out in the presence of one equivalent of trimethylamine. The resultant $^{31}P-\{^1H\}$ n.m.r. spectrum showed $PtCl(PEt_3)_2(PCl_2)$ to be the only product at 200 K. Removing the cold tube from the probe of the n.m.r. machine and cooling to 176 K resulted in the precipitation of a white material insoluble at this temperature. Isolation of this product allowed it to be identified as $Me_3N^+Cl^-$. Attempts at isolating $PtCl(PEt_3)_2(PCl_2)$ are discussed in chapter 2 and a study of its reactions is detailed in chapters 4 and 5. The

formation of $PtCl_2H_2(PEt_3)_2$ is also inhibited by reacting $PtClH(PEt_3)_2$ with a very large excess of PCl_3.

Attempts to detect the six-coordinate precursor were unsuccesful, even when a mixture of diethylether and dichloromethane was used as solvent, allowing the $^{31}P-\{^1H\}$ n.m.r. spectrum to be recorded at 150 K. The instability of six-coordinate platinum(IV) intermediates is not uncommon and no further attempts were made to detect this precursor.

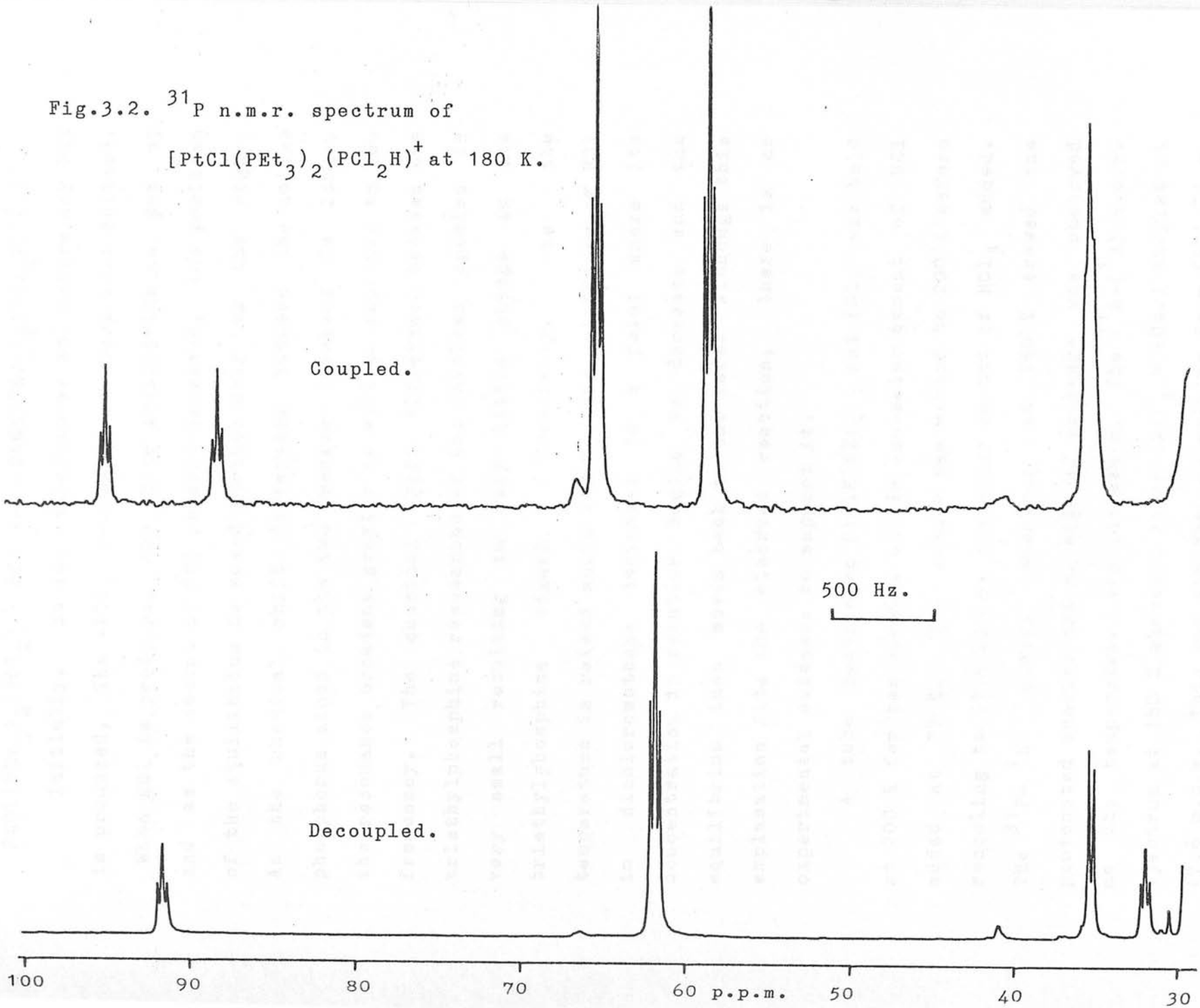
Further warming the sample above 180 K resulted in the high frequency resonance broadening, shifting to lower frequency and losing structure. The broadening was not symmetrical; the centre line and the high frequency satellite could be distinguished, but the low frequency satellite could not. The change in the triethylphosphine resonance was minimal and the PP' coupling was still visible. This broadening and shifting to lower frequency of the unique phosphorus resonance continued as the temperature was raised towards 240 K. Above this temperature, however; even slight increases in temperature resulted in the process reversing, and by 250 K the resonance had returned to its original position and associated sharpness. Recooling the sample showed this process to be completely reversible. These observations are consistent with an exchange process between two species whose triethylphosphine resonances occur at similar chemical shifts. The chemical shifts of their unique phosphorus resonances, however, must be radically different. The chemical shift of the new

species must be to low frequency of that of the initial species in order to account for the observed pattern of broadening. Allowing the chemical shift of this resonance to reach its lowest value and then restoring the proton coupling to the spectrum resulted in the resonance splitting into a wide doublet. The size of this coupling was indicative of a four-coordinate phosphorus. The implication of this is that the unique phosphorus of $PtCl(PEt_3)_2(PCl_2)$ is being reversibly protonated. The shift to low frequency is as would be expected upon protonation of the unique phosphorus.

In an attempt to verify this hypothesis, a tube was prepared containing $PtClH(PEt_3)_2$ and PCl_3 and held at 200 K for five minutes to allow the product to form. One equivalent of HCl was then added at 77 K and the tube sealed and placed in the probe of the n.m.r. machine. The $^{31}P-\{^1H\}$ n.m.r. spectrum at 180 K showed a narrow triplet with platinum satellites centered at +62.7 p.p.m. Retention of proton coupling split this into a wide doublet as previously observed (fig.3.2). The triethylphosphine region showed a corresponding narrow doublet with platinum satellites whose chemical shift was very similar to that of the $-PCl_2$ species.

These observations imply that that HCl is being produced in the reaction between $PtClH(PEt_3)_2$ and PCl_3 which is protonating the $-PCl_2$ group of the product. As the protonation is reversible, this indicates that an equilibrium between HCl, $PtCl(PEt_3)_2(PCl_2)$ and the protonated species is involved.

Fig.3.2. ^{31}P n.m.r. spectrum of $[PtCl(PEt_3)_2(PCl_2H)]^+$ at 180 K.



$PtCl(PEt_3)_2(PCl_2) + HCl \text{ -- } [PtCl(PEt_3)_2(PCl_2H)]^+Cl^-$

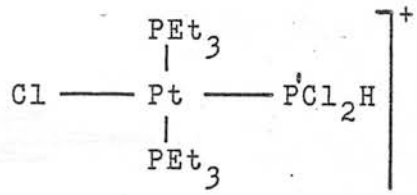
Initially, at low temperatures and before any HCl is produced, The $-PCl_2$ resonance is sharp well defined. When HCl is produced, the above equilibrium is set up and as the amount of HCl present increses, the position of the equilibrium is moved further over to the right. As the chemical shift difference between the unique phosphorus atoms in the two species involved is large, the resonance broadens greatly as well as shifting to low frequency. The chemical shift difference between the triethylphosphine resonances of the involved species is very small resulting in very little change in the triethylphosphine signal. Presumably, as the temperature is raised above 240 K, the solubility of HCl in dichloromethane decreases to a point where its concentration in solution begins to decrease and the equilibrium then moves back to the left. Although this explanation fits the observed reaction, there is no experimental evidence to support it.

A tube containing $PtClH(PEt_3)_2$ and PCl_3 was held at 200 K for ten minutes and an equimolar amount of HCl added at 77 K. The sample was warmed to 200 K before recooling to 77 K and an equimolar amount of BCl_3 added. THe $^{31}P-{}^{1}H$ n.m.r. spectrum at 180 K showed the protonated species and no sign of exchange was observed as the temperature was increased. The $^{11}B-\{^{1}H\}$ n.m.r. spectrum at 180 K showed a sharp ($W1/_2$ = 2Hz.) singlet at +7.6 p.p.m. This was assigned as arising from $[BCl_4^-]$ on the basis of its chemical shift and line width.[6] The ^{1}H

nmr spectrum (fig.3.3) at this temperature showed a wide doublet of triplets with platinum satellites which was attributed to the $PCl_2\underline{H}$ resonance.

Increasing the concentration of either , or both, HCl or BCl_3 in this reaction had no further effect on the parameters of the species and it was assumed that the product was in the completely protonated form.

There seems no doubt that the species is



$\delta P = +23.0$ p.p.m. $\quad \delta P' = +62.7$ p.p.m.

$\delta H = +8.69$ p.p.m. $\quad {}^1J_{PtP} = 1943$ Hz.

${}^1J_{PtP'} = 4750$Hz. $\quad {}^1J_{P'H} = 550$ Hz.

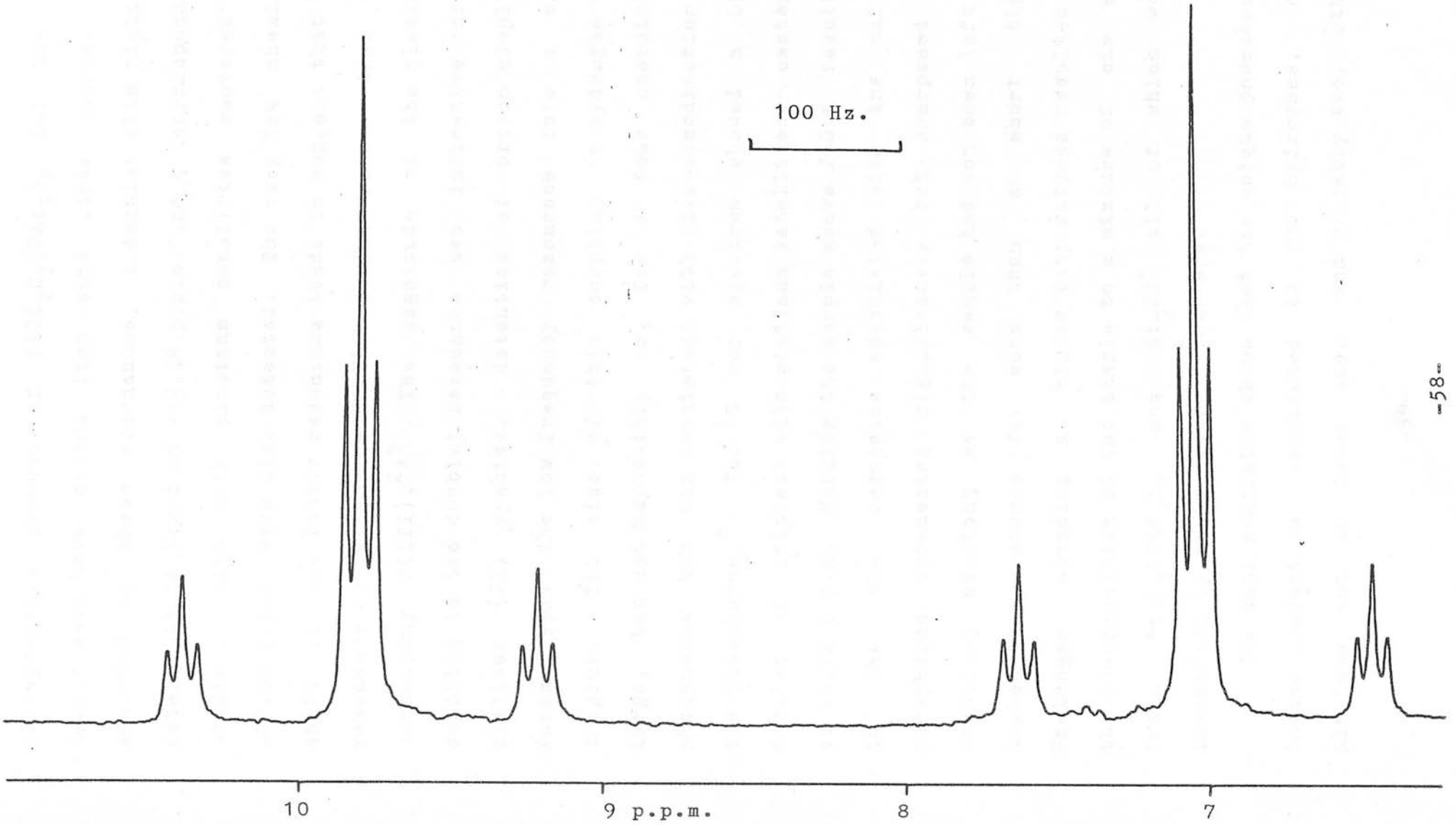
${}^2J_{PP'} = 23$ Hz. $\quad {}^2J_{PtH} = 235$ Hz.

${}^3J_{PH} = 9$ Hz.

All parameters were recorded in dichlomethane at 180 K and are for the species produced in the presence of BCl_3.

Further warming of a tube containing stoichiometric amounts of $PtClH(PEt_3)_2$ and PCl_3 above 240 K resulted in the resonances due to $PtCl(PEt_3)_2(PCl_2H)^+$ and $PtCl_2H_2(PEt_3)_2$ slowly dissapearing and several new resonances appearing. Two singlets with platinum satellites were identified from their chemical shifts and coupling constants as being due to cis and trans $PtCl_2(PEt_3)_2$. The trans isomer may have arisen as the

Fig.3.3. ^{1}H n.m.r. spectrum of $[PtCl(PEt_3)_2(PCl_2H)]^+$ at 180 K.



decomposition product of $PtCl_2H_2(PEt_3)_2$ but the cis isomer must have arisen from some other source. In addition to these resonances, a doublet with platinum satellites centered at +12.48 p.p.m. and a corresponding triplet, also with platinum satellites centered at -71.00 p.p.m. were also detected. The very low chemical shift of the latter resonance tends to suggest that the resonance arose from a P(V) species rather than one containing P(III).[2,7] The magnitude of the platinum coupling to the doublet resonance was indicative of a platinum (II) species. Retention of proton coupling further split the low frequency resonance into a wide triplet. The size of this coupling to hydrogen was large, but not impossibly so, for a four coordinate phosphorus but was consistent with five-coordination at the phosphorus.[8] The ^1H nmr spectrum showed a wide doublet of triplets with platinum satellites, centered at +6.22 p.p.m. Warming the sample above 260 K resulted in the the resonance associated with the unique phosphorus broadening significantly but sharpened on recooling as long as the sample had not been left at higher temperatures for more than a short time. Prolonged standing at higher temperatures resulted in the decomposition of the sample to a mixture of cis and trans $PtCl_2(PEt_3)_2$ and Et_3PH^+ all of which were identified by their n.m.r. parameters.

The data available shows that the unique phosphorus in the product is coordinated to two hydrogens, one platinum and at least one, and probably two, other

ligands. The(se) other ligand(s) have to be chloride in the absence of any other alternatives. This presents two possible structures for this species. The first is the neutral species containing a coordinated (PH_2Cl_2) group and the second is the cationic species containing a coordinated (PH_2Cl) group:

$PtCl(PEt_3)_2(P'H_2Cl_2)$ OR $[PtCl(PEt_3)(P'H_2Cl)]^+Cl^-$

Due to the ambiguity caused by the size of the coupling between hydrogen and the unique phosphorus, it was not possible to establish which of these structures was correct on the basis of the data obtained from this experiment. Other experiments were carried out in order to ascertain the nature of the product. Reaction of a 1:1:1 mixture of $PtClH(PEt_3)_2$, PCl_3 and BCl_3 resulted in the formation of the protonated $-PCl_2$ species. Reaction of a 1:1:4 mixture of $PtClH(PEt_3)_2$, PCl_3 and HCl had the same result. A tube, fitted with a breakseal, was prepared with equimolar amounts of $PtClH(PEt_3)_2$ and PCl_3 as described in chapter 2. The reaction was then monitored by $^{31}P-\{^1H\}$ n.m.r. until a significant amount of "$PtCl(PEt_3)_2(P'H_2Cl_2)$" had formed. The tube was then removed from the instrument and an equimolar amount of BCl_3 (based on the amount of platinum used) added at 77 K.

The $^{31}P\{^1H\}$ n.m.r. spectrum at 230 K showed a dramatic change to have occurred. The unique phosphorus resonance at -70.0 p.p.m. had been replaced by a new triplet with platinum satellites centered at -16.1 p.p.m. The triethylphosphine resonance of the original species

had been replaced by a new doublet, also with platinum satellites, centered at +17.34 p.p.m. The magnitude of the platinum coupling to the latter resonance again showed the species to contain four-coordinate platinum(II). Retention of proton coupling split the low frequency resonance into a further wide doublet (fig.3.4). The proton coupling of 487 Hz. was unquestionably attributable to a species containing a four-coordinate phosphorus. The $^{11}B-\{^{1}H\}$ n.m.r. spectrum showed a singlet at +7.4 p.p.m. which is within experimental error of the literature value for $[BCl_4^-]$. The width at half height of the resonance was greater than normal at 20 Hz. but may have been a consequence of the temperature. The value of the coupling between the unique phosphorus and platinum was also reduced. The ^{1}H nmr spectrum showed a wide doublet of triplets with platinum satellites centered at +6.38 p.p.m.

It appears that the BCl_3 has acted as a chloride acceptor by removing a chloride from the unique phosphorus. As the unique phosphorus in this product is known to be four-coordinate and that as chloride has been removed, the implication is that, prior to BCl_3 addition, it must have been five-coordinate. This suggests that an equilibrium exists between the two species. ie.

$$PtCl(PEt_3)_2(P'H_2Cl_2) \rightleftharpoons [PtCl(PEt_3)(P'H_2Cl)]^+Cl^-$$

Addition of BCl_3 coordinates the Cl^- and hence drives the equilibrium to the right.

Another similar experiment was set up using the

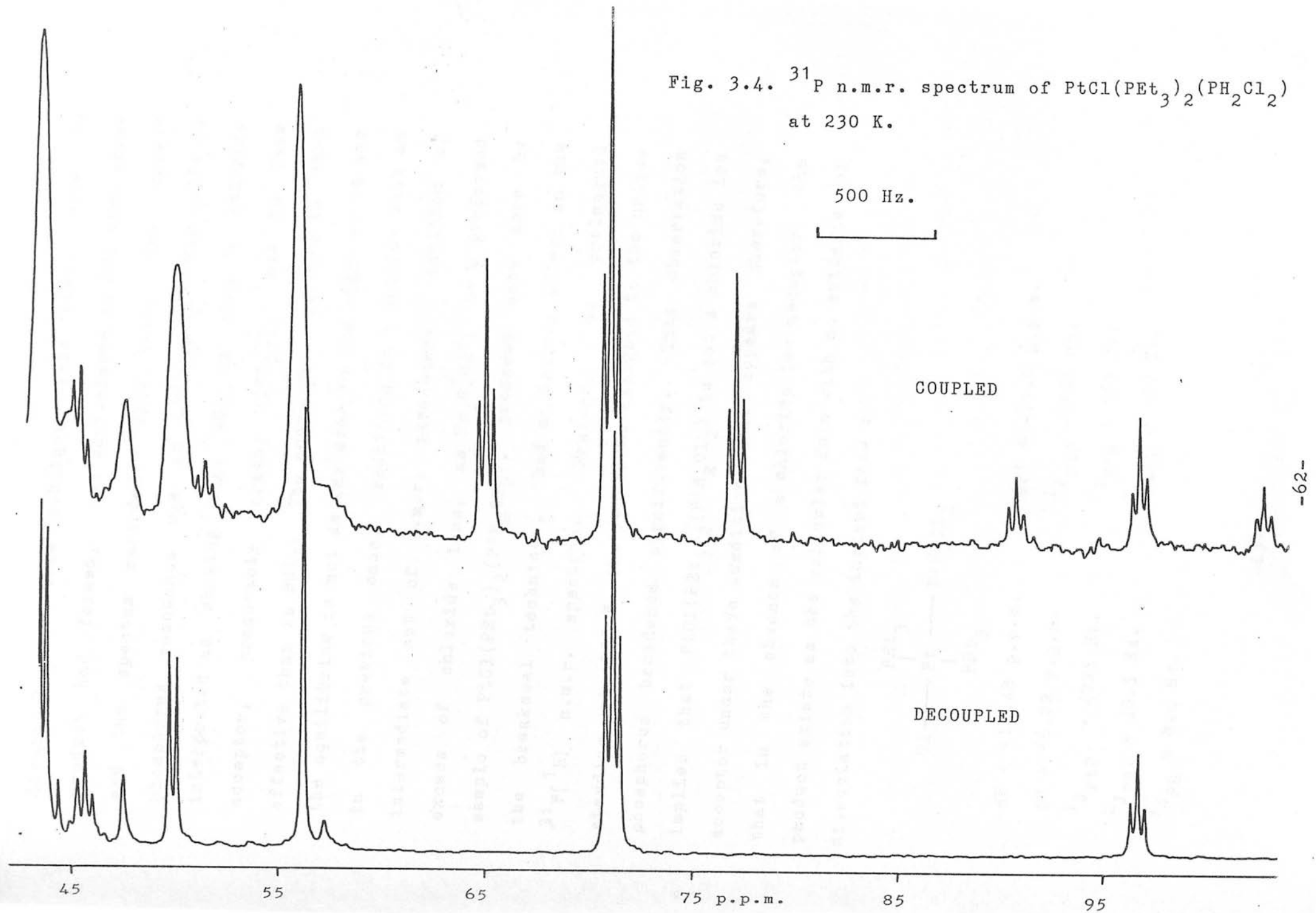
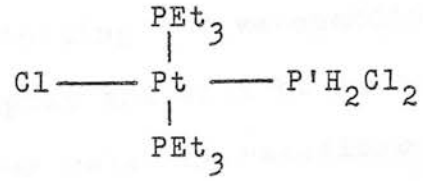


Fig. 3.4. ^{31}P n.m.r. spectrum of $PtCl(PEt_3)_2(PH_2Cl_2)$ at 230 K.

breakseal n.m.r. tube technique. This time, once the product had formed, two equivalents of HCl were added and the spectum recorded. This time, the unique phosphorus resonance was at -36 p.p.m. The shift is interpreted as showing that HCl is also a chloride acceptor, presumably forming $[HCl_2^-]$, but is less effective than is BCl_3. The consequence of this is that the equilibrium is not as far over to the right as it was in the previous case, resulting in a species with an intermediate set of n.m.r. parameters. Addition of excess of chloride ions, as $Pr_4N^+Cl^-$, to a preformed sample of $PtCl(PEt_3)_2(P'H_2Cl_2)$, produced once more by the breakseal technique, had no initial effect on the $^{31}P\{^1H\}$ n.m.r. spectrum. However, on prolongued standing at 220 K the resonance assigned to the unique phosphorus broadened significantly. This observation implies that $PtCl(PEt_3)_2(P'H_2Cl_2)$ is not a chloride ion acceptor under these conditions. It appears therefore, that in the absence of a chloride ion acceptor, the product exists as the molecular form with no evidence of dissociation into the ionised form :-



$\delta P = +12.48$ p.p.m. $\quad \delta P' = -71.0$ p.p.m.

$\delta H = +6.22$ p.p.m. $\quad {}^1J_{PtP} = 2135$ Hz.

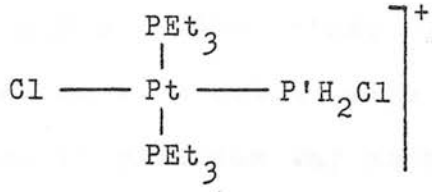
${}^1J_{PtP'} = 4725$ Hz. $\quad {}^1J_{P'H} = 555$ Hz.

${}^2J_{PP'} = 30.5$ Hz. $\quad {}^2J_{PtH} = 109$ Hz.

${}^3J_{PH} = 8.4$ Hz.

All parameters were recorded in dichlomethane at 230 K.

However, in the presence of a chloride ion acceptor such as BCl_3, the cationic form exists



δP = +17.34 p.p.m. $\delta P'$ = -16.14 p.p.m.

δH = +6.38 p.p.m. $^1J_{PtP}$ =1989 Hz.

$^1J_{PtP'}$ = 4121 Hz. $^1J_{P'H}$ = 487 Hz.

$^2J_{PP'}$ = 29.5 Hz. $^2J_{PtH}$ = 112 Hz.

$^3J_{PH}$ = 9.2 Hz.

All parameters were recorded in dichloromethane at 230 K and are from a sample which had one equivalent of BCl_3 added to drive the equilibrium fully to the right; addition of larger amounts of BCl_3 did not cause any further change in the parameters so it was assumed that these values represent the limiting case of the equilibrium.

The mechanism of formation of these species containing five-coordinate phosphorus(V) groups is complex and will be discussed later in the chapter once other relevant reactions have been described.

3.3. Reaction of $PtBrH(PEt_3)_2$ with PBr_3.

The reaction was carried out using stoicheiometric amounts of reagents. Reaction was again rapid and

observing the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at the melting point of the solvent revealed two very high frequency resonances (fig.3.5). The resonance to higher frequency was a triplet with platinum satellites, centered at +320.2 p.p.m. The other signal in this region was analysed as a triplet with platinum satellites. The coupling to platinum was much smaller in this signal with the result that the satellites partially overlapped the central resonance, taken as a hopeful sign that the platinum may have been six-coordinate. This resonance was centered at +277.0 p.p.m. Retention of proton coupling had no effect on either of these resonances. A signal at +218 p.p.m. was assigned as arising from excess PBr_3. The triethylphosphine region of the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed a singlet with platinum satellites which was identified on the basis of its parameters as due to $PtBr_2H_2(PEt_3)_2$. In addition to this resonance, two narrow doublets, both with platinum satellites, were observed. The doublet couplings matched the triplet couplings observed in the high frequency signals. The higher frequency doublet, corresponding to the higher frequency triplet, showed a coupling to platinum which was indicative of a four-coordinate platinum(II) species. By analogy with the reaction described in the preceding section, this species was assigned the structure

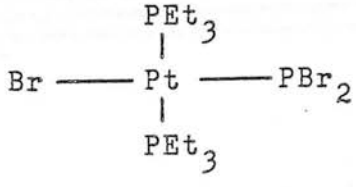
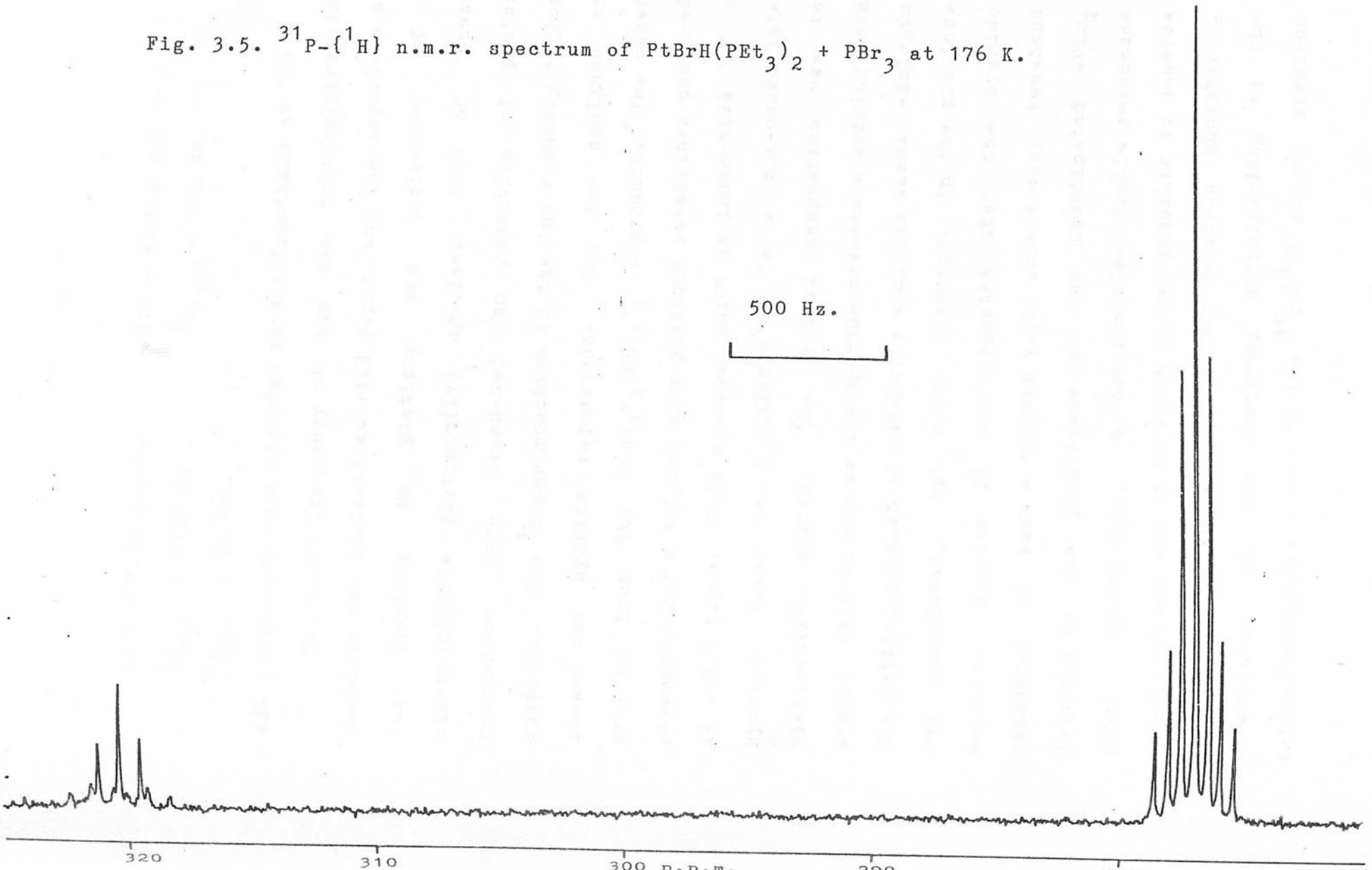


Fig. 3.5. $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $PtBrH(PEt_3)_2 + PBr_3$ at 176 K.



δP = +17.70 p.p.m. $\delta P'$ = +320.2 p.p.m.

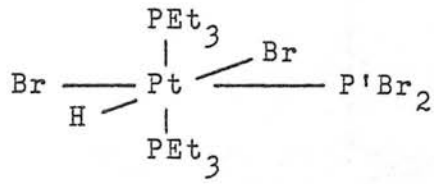
$^1J_{PtP}$ = 2132 Hz. $^1J_{PtP'}$ = 186 Hz.

$^2J_{PP'}$ = 70 Hz.

All parameters were recorded in dichlomethane at 176 K.

The lower frequency of the two triethylphosphine doublets was centered at +4.3 p.p.m. and the magnitude of its coupling to platinum was indicative of a six-coordinate platinum(IV) species. Both of these resonances were broadened on retention of proton coupling. The ^1H nmr spectrum of the low requency region showed two hydride resonances. One was assigned as arising from the $PtBr_2H_2(PEt_3)_2$ biproduct. The other resonance was a triplet with platinum satellites centered at -15.0 p.p.m. This chemical shift is indicative of a hydride trans to a halogen[4,9] in a six-coordinate platinum(IV) system. The initial temptation was to assign this as due to the hydride resonance arising from the initial product of oxidative addition whose analogue was postulated, but never observed, in the previous section. However it was expected that the hydride resonance of such a species would show a cis, two-bond coupling to the phosphorus of the coordinated $-PBr_2$ group. Accordingly, a heteronuclear double resonance experiment was set up in which it was possible to observe the ^1H nmr spectrum and selectively decouple phosphorus. Irradiation at the frequency corresponding to the triethylphosphine signal in the $^{31}P-\{^1H\}$ n.m.r. spectrum

collapsed the triplet coupling in the hydride resonance (fig.3.6) showing that these resonances arose from the same molecule. Thus, this species was assigned as being the product of the initial oxidation whose analogue was postulated, but not observed, in the preceding section.



$\delta P = +4.3$ p.p.m. $\quad \delta P' = +277.0$ p.p.m.

$\delta H = -15.04$ p.p.m. $\quad {}^{1}J_{PtP} = 1741$ Hz.

${}^{1}J_{PtP'} = 167$ Hz $\quad {}^{1}J_{PtH} = 798$ Hz.

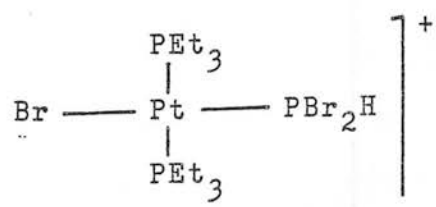
${}^{2}J_{PP'} = 45$ Hz. $\quad {}^{2}J_{P'H}$ = n.o.

n.o. means not observed.

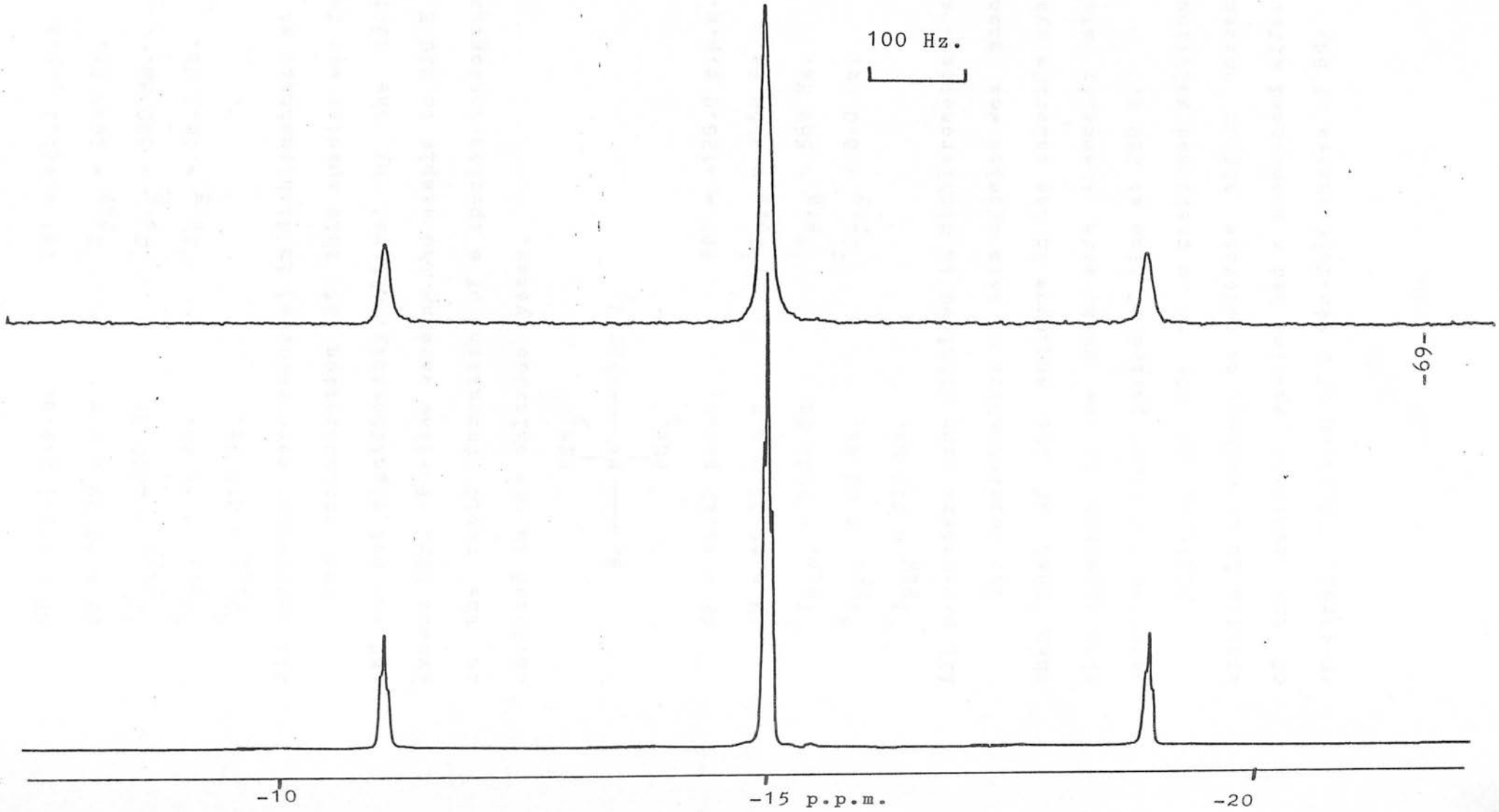
All parameters were recorded in dichlomethane at 180 K.

Warming the sample above 190 K resulted in the loss of signals associated with this species and raising the temperature a further 10 K resulted in the loss of signals associated with the four-coordinate $-PBr_2$ species.

Further warming resulted in analogous behaviour to that observed in the chloride system and small amounts of the species assigned as being the protonated species formed.



^{31}P n.m.r. spectrum selective decoupling experiment at 176 K.



$\delta P = +15.5$ p.p.m. $\quad \delta P' = +42.2$ p.p.m.

$\delta H = +8.29$ p.p.m $\quad {}^{1}J_{PtP} = 2083$ Hz.

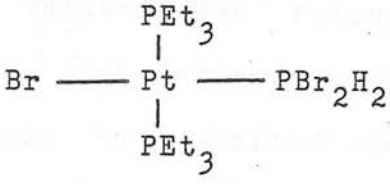
${}^{1}J_{PtP'} = 4830$ Hz $\quad {}^{1}J_{P'H} = 500$ Hz.

${}^{2}J_{PP'} = 24$ Hz. $\quad {}^{2}J_{P'H} = 10.5$ Hz.

${}^{2}J_{PtH} = 218$ Hz.

All parameters were recorded in dichlomethane at 180 K.

The concentration of this species was fairly low and was not significantly altered by the addition of excess HBr. Further warming the sample to 220 K resulted in the rapid formation of a species analogous to that obtained in the chloride system.



$\delta P = +4.22$ p.p.m. $\quad \delta P' = -128.0$ p.p.m.

$\delta H = +5.83$ p.p.m $\quad {}^{1}J_{PtP} = 2168$ Hz.

${}^{1}J_{PtP'} = 5002$ Hz $\quad {}^{1}J_{P'H} = 569$ Hz.

${}^{2}J_{PP'} = 28$ Hz. $\quad {}^{2}J_{P'H} = 8.0$ Hz.

${}^{2}J_{PtH} = 117$ Hz.

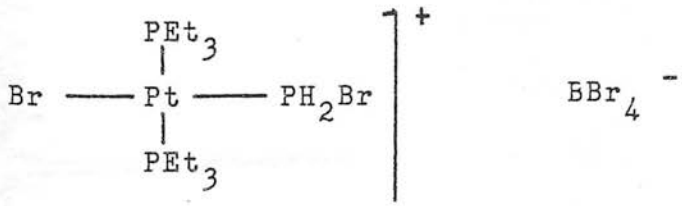
All parameters were obtained in dichloromethane at 220 K

The concentration of this species was much higher than that of its analogue in the chloride system. It also appeared to be much more thermally stable and survived for short period of time at 280 K.

Addition of HBr to a preformed solution of this species in an attempt to generate higher concentrations of the cationic species had a pronounced affect on the spectrum. Addition of a two-fold excess of HBr resulted

in the chemical shift of the unique phosphorus resonance moving from -128 p.p.m. to -65.6 p.p.m. Addition of a four-fold excess of HBr moved the resonance to -60.9 p.p.m. with correspondingly large decreases in the coupling to platinum and smaller changes in the other parameters (fig.3.7).

In an attempt to determine if this was the limiting value for this species, the reaction of the $-PH_2$ Br_2 species with BBr_3 was studied. Addition of one equivalent of BBr_3 (based on the amount of platinum initially used) to a preformed solution of the $-PH_2Br_2$ species gave rise to $^{31}P-\{^1H\}$ n.m.r. spectrum which showed several unidentified resonances but also large concentrations of the desired cationic species. The unique phosphorus had shifted to -53.5 p.p.m. with corresponding reductions in the couplings to both platinum and hydrogen. The other parameters had also altered but to a lesser extent. Observing the $^{11}B-\{^1H\}$ n.m.r. spectrum showed a fairly sharp ($W1/_2$ = 7Hz.) resonance at -23.3 p.p.m. which was assigned[6,10] as arising from $[BBr_4]^-$. Addition of higher concentrations of BBr_3 did not alter the n.m.r. parameters significantly and this was taken to be the limiting case for this species and its identity was assigned as



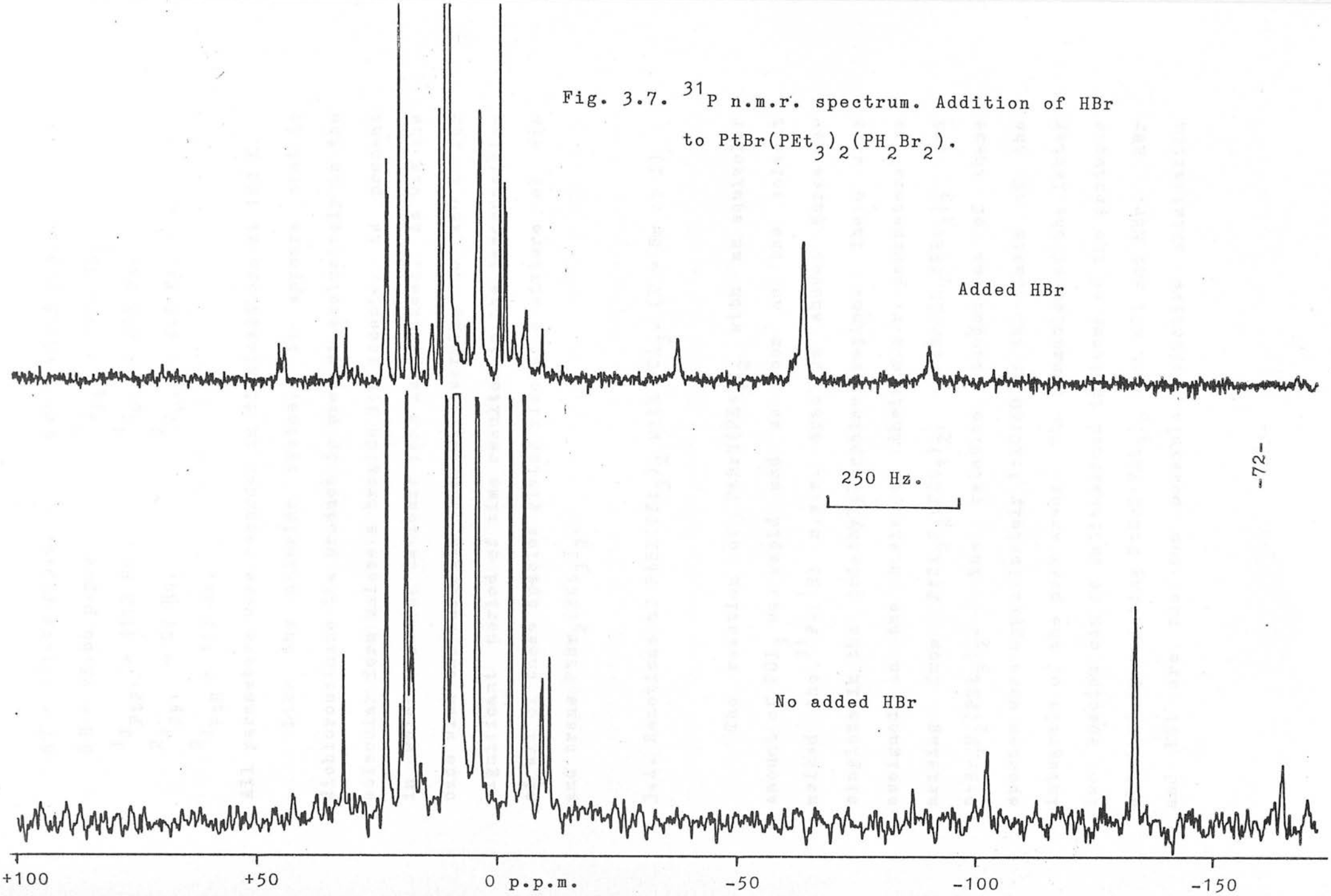


Fig. 3.7. ^{31}P n.m.r. spectrum. Addition of HBr to $PtBr(PEt_3)_2(PH_2Br_2)$.

$\delta P = +11.83$ p.p.m. $\delta P' = -53.5$ p.p.m.

$\delta H = +5.66$ p.p.m $^1J_{PtP} = 1974$ Hz.

$^1J_{PtP'} = 4112$ Hz $^1J_{P'H} = 485$ Hz.

$^2J_{PP'} = 27$ Hz. $^2J_{P'H} = 8.8$ Hz.

$^2J_{PtH} = 113$ Hz.

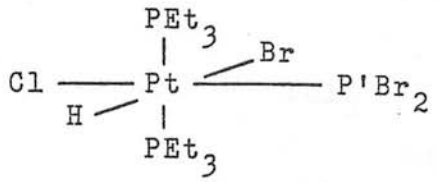
All parameters were recorded in dichlomethane at 180 K.

Like the chloride system, it appears that in dichloromethane the product is present exclusively in the molecular form unless a bromide ion acceptor is present in which case the cationic form is produced. As was the case with the chloride system, warming to 280 K for significant period of time resulted in the decomposition of all of these species giving rise to a mixture of cis and trans $PtBr_2(PEt_3)_2$.

3.4. Reactions of $PtHX(PEt_3)_2$ with PCl_3. (X = Br or I)

The reaction of $PtBrH(PEt_3)_2$ with an equimolar amount of PCl_3 was rapid and as soon as the solvent melted the $^{31}P-\{^1H\}$ n.m.r. spectrum showed three new singlets in the triethylphosphine region. These were assigned on the basis of their n.m.r. parameters[4] as arising from $PtCl_2H_2(PEt_3)_2$, $PtBrClH_2(PEt_3)_2$ and $PtBr_2H_2(PEt_3)_2$. The relative abundancies of these species were approximately 1:40:40 on the basis of the integrals of the peak areas. The formation of the latter two species can be rationalised in terms of the products obtained by reacting $PtBrH(PEt_3)_2$ with HCl and HBr. HBr and HCl are the two possible reductive elimination

products from the initial six-coordinate product of the main reaction. i.e.

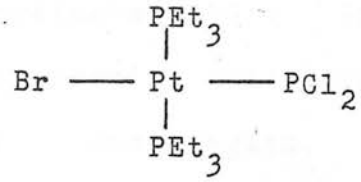


- or an isomer thereof.

The formation of $PtCl_2H_2(PEt_3)_2$ is not so simple to rationalise but presumably arises from an exchange process at platinum.

In addition to these simple products, two narrow doublets with platinum satellites were also obseved. The high frequency region showed two narrow triplets, also with platinum satellites. On the basis of the different PP' couplings, it was possible to relate each of these to its corresponding doublet. The ^1H nmr spectrum showed no low frequency hydrides other than those attributable to the six-coordinate species above. The more intense of the two pairs of doublets and triplets in the $^{31}P-\{^1H\}$ n.m.r. spectrum was assigned as arising from $PtCl(PEt_3)_2(PCl_2)$ on the basis of the parameters obtained earlier. The other sets of resonances had similar, although slightly smaller, parameters to those obtained from $PtCl(PEt_3)_2(PCl_2)$. The platinum was again four-coordinate. The two possible candidates for the structure of this species were thought to be $PtBr(PEt_3)_2(PCl_2)$ and $PtCl(PEt_3)_2(PBr_2)$. By comparison of the parameters obtained from $PtCl(PEt_3)_2(PBr_2)$ it was decided unlikely that this species cotained a terminal

$-PBr_2$ group. On this basis, the structure of the species was assigned as



$\delta P = +18.3$ p.p.m. $\delta P' = +307.0$ p.p.m.

$^1J_{PtP} = 2630$Hz. $^1J_{PtP'} = 370$ Hz.

$^2J_{PP'} = 59$ Hz.

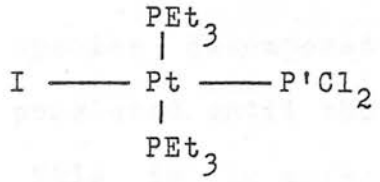
All parameters were recorded in dichlomethane at 180 K.

On the assumption that the initial product of the reaction was indeed the species postulated earlier, it is in keeping with the general behaviour of platinum that HCl would be the reductively eliminated molecule, leaving the heavier halogen still bound to platinum. Although this accounts for the formation of the species above, it does not explain the formation of $PtCl(PEt_3)_2(PCl_2)$, nor does it account for the formation of equal concentrations of $PtBr_2H_2(PEt_3)_2$ and $PtBrClH_2(PEt_3)_2$. This suggests that some fairly complex exchange processes have been involved in the formation of this reaction mixture.

Warming the the sample above this temperature resulted in further reactions occuring which made the spectra so complex that no further interpretation was possible. In view of the limited interest in this system , it was decided not to pursue the reaction any further.

Reaction between $PtHI(PEt_3)_2$ and PCl_3 was very

similar to the above reaction except that the $^{31}P-\{^{1}H\}$ n.m.r. spectrum failed to show any $PtCl_2H_2(PEt_3)_2$. The relative abundancies of $PtI_2H_2(PEt_3)_2$ to $PtClIH_2(PEt_3)_2$ was approximately 10:1. In addition to these species, two other species containing unique phosphorus atoms were detected. Once again, the more abundant of them was assigned the structure $PtCl(PEt_3)_2(PCl_2)$. The other species was assigned as containing a $-PCl_2$ group on the basis of its n.m.r. parameters and its structure was asigned as



$\delta P = +13.4$ p.p.m. $\quad \delta P' = +298.0$ p.p.m.

$^{1}J_{PtP} = 2622$ Hz. $\quad ^{1}J_{PtP'} = 246$ Hz.

$^{2}J_{PP'} = 59.9$ Hz.

All parameters were recorded in dichlomethane at 180 K. It is interesting to note the dramatic change in the value of the platinum coupling to the unique phosphorus as the size of the trans halogen is increased. Further warming had the same result as in the bromide system and no further interpretation was possible.

3.5. Reactions involving excess $PtHX(PEt_3)_2$.

(X = Cl or Br)

The reaction between excess $PtClH(PEt_3)_2$ and PCl_3 in dichloromethane was much simpler than in the case of

the stoicheiometric rection. The only products detected in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum up to 300 K were $PtCl(PEt_3)_2(PCl_2)$, $PtCl_2H_2(PEt_3)_2$ and unreacted $PtClH(PEt_3)_2$. No further reaction was observed even on prolongued standing.

The reaction between PBr_3 and excess $PtBrH(PEt_3)_2$ was more complex. As soon as the solvent melted, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed resonances which were attributable to unreacted $PtBrH(PEt_3)_2$, $PtBr_2H_2(PEt_3)_2$, $PtBr_2H(PEt_3)_2(PBr_2)$ and $PtBr(PEt_3)_2(PBr_2)$. As soon as the temperature was raised to 180 K, the six-coordinate $-PBr_2$ species decomposed but the four-coordinate $-PBr_2$ species persisted until the temperature was raised above 250 K. This is in marked contrast to its behaviour in the stoichiometric reaction. Further warming, and removing the tube from the probe to shake it briefly, resulted in the appearance of further resonances, attributable to cis and trans $PtBr_2(PEt_3)_2$. In addition to these, a doublet and triplet were observed, both with satellites and both in the triethylphosphine region. These were assigned as arising from $[PtH(PEt_3)_3]^+$. A small amount of $[PtBr(PEt_3)_2(PH_2)PtBr(PEt_3)_2]^+$ was identified by its n.m.r. parameters[11]. The process whereby this species is formed can be rationalised on the basis of reaction of the molecular form of $PtBr(PEt_3)_2(P'H_2Br_2)$. If Br_2 is transferred from the unique phosphorus of this species to excess $PtBrH(PEt_3)_2$ giving rise to $PtBr(PEt_3)_2(P'H_2)$, then this product could be envisaged displacing Br^- from $PtBr_2(PEt_3)_2$ hence

forming the $-PH_2$ bridged species. This can also be taken as further proof of the structure of the species formulated as containing a $-PH_2Br_2$ group. If the structure was in the cationic form, to formulate an analogous mechanism for the formation of the $-PH_2$ bridged species relies on the displacement of Br^+. This seems to be unlikely, particularly as the cationic form was produced by displacement of Br^- from the molecular form.

3.6. Attempts to fluorinate the unique phosphorus of $PtBr(PEt_3)_2(P'H_2Br_2)$.

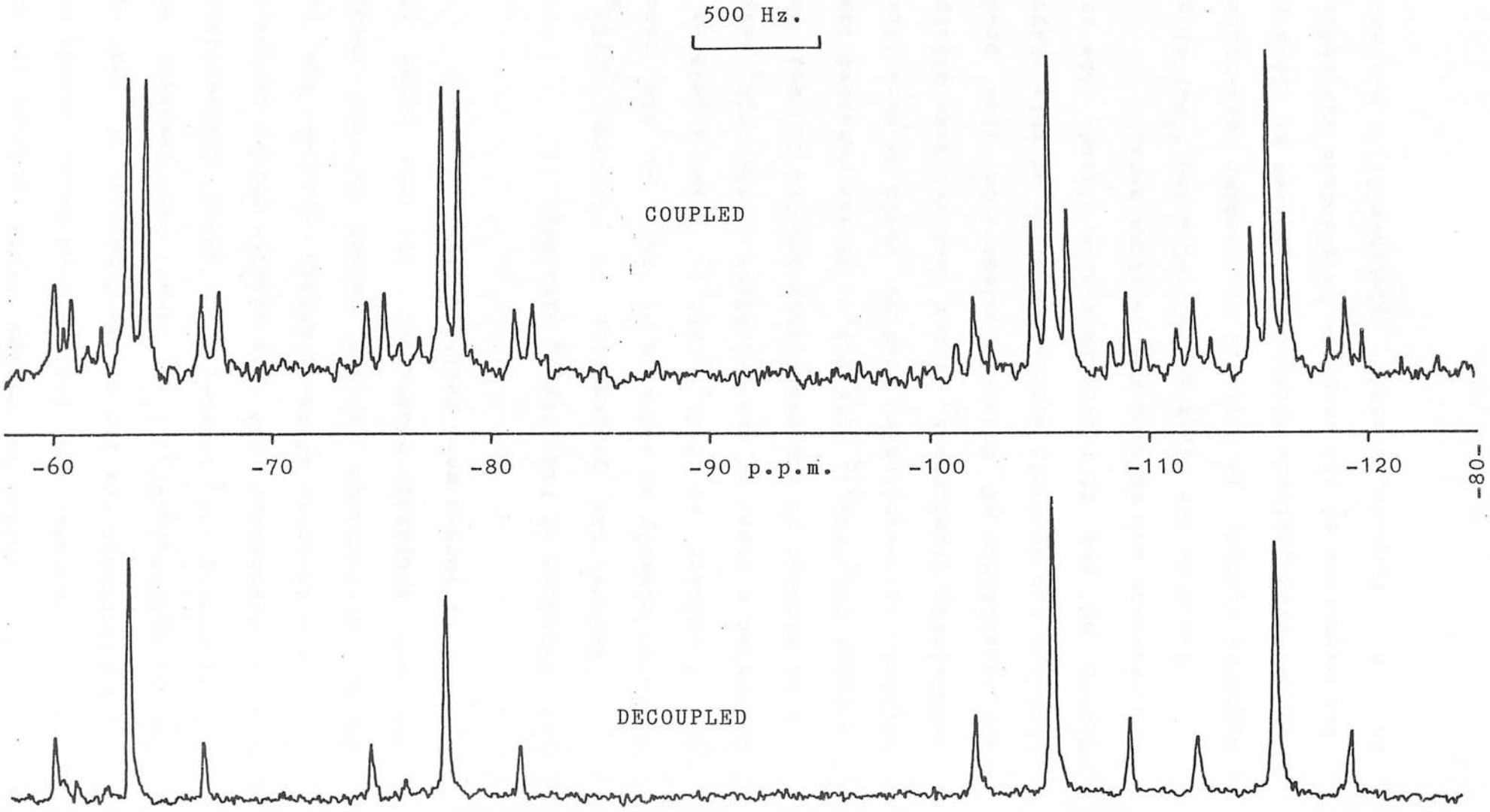
Although the n.m.r. experiments with HX and BX_3 have proven that the final interesting product in the reaction between $PtHY(PEt_3)_2$ and PX_3 contains a five-, rather than four-coordinate unique phosphorus, there is still a slight doubt that it could six-coordinate. This would result in the anionic species $PtX(PEt_3)_2(P'H_2X_3)^-$. This is thought to be rather unlikely in the light of the size of the one bond coupling between phosphorus and hydrogen. The absence of an obvious cation also causes problems. Partly because of this slight doubt and also that the species would be novel, it was decided to attempt to produce the species containing a coordinated $-PH_2F_2$ group.

It was decided to carry out the fluorination reactions on the bromo system in view of its relative stability and ease of formation. The reaction with SbF_3 resulted in the rapid decomposition of the

$PtBr(PEt_3)_2(P'H_2Br_2)$. Solubility problems ruled out a number of the normal fluorinating reagents so fluorotrimethyl germane was chosen as a likely mild fluorinating agent. The volatility of this reagent also helped to simplify the experiment.

The reaction was carried out with a four-fold excess of Me_3GeF relative to the amount of platinum used initiallly. The results were complex and a wide range of products was obtained. It was difficult to analyse which species were formed from the Me_3GeF because as soon as the temperature rose above 190 K, PF_3 was formed in substantial amounts. The products included a four-coordinate platinum species which had a PF_3 group cis to a hydride yet contained only one triethylphosphine ligand. The desired product could not be detected but the complexity of the spectrum made interpetation very difficult. Observing the $^{19}F\{^1H\}$ n.m.r. spectrum showed two very weak sets of resonaces which were of interest. Both sets were doublets with platinum satellites centered at -72.9 and -112.1 p.p.m. Retention of proton coupling further split the higher frequency signal into a doublet and the lower frequency signal into a triplet (fig.3.8). In both cases, the coupling to hydrogen was 60 Hz. The phosphorus - fluorine couplings were indicative of four- and five-coordinate phosphorus centres respectively. These observations are consistent with $-PHF_2$ and $-PH_2F_2$ groups coordinated to platinum. The absence of any coupling to triethylphosphine groups and the failure to locate the corresponding phosphorus signals meant that it

Fig. 3.8. ^{19}F n.m.r. spectrum $PtBr(PEt_3)_2(PH_2Br_2)$ + Me_3GeF at 210 K.



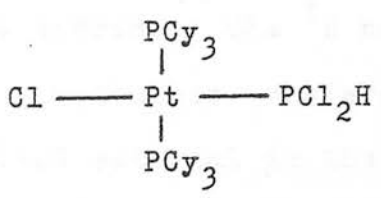
was not possible to assign these resonances to the desired species and its cationc form. Recent work in this department has led to the formation of the species $Ir(CO)Cl_2(PEt_3)_2(PF_2H_2)$[11] from the reaction of the corresponding $-PH_2$ species with xenon difluoride. The n.m.r. parameters for this species places severe doubts as to the identity of the platinum species due to the large differences in the values of the phosphorus fluorine coupling constants. At this point it was decided to pursue more fruitful lines of work.

3.7. Reaction of $PtH_2(PCy_3)_2$ with PCl_3.

Before the preparation of $PtCl(PEt_3)_2(PCl_2)$ was achieved cleanly by addition of Me_3N to the reaction, the formation of $PtCl_2H_2(PEt_3)_2$ posed a problem which prevented a study of the reactions of the $-PCl_2$ compound. In an attempt to circumvent this problem it was decided to react $PtH_2(PCy_3)_2$ with PCl_3. It was reasoned that the initial six-coordinate product would be more likely to reductively eliminate H_2 rather than HCl thus eliminating the possibility of forming undesirable side products. Although not strictly within the title of this chapter by virtue of the different phosphine ligand, the results are relevant and as such are detailed here.

Reaction was rapid and at 180 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed, in addition to starting materials, a doublet with platinum satellites centered at +39.6 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) center. A

corresponding triplet with platinum satellites was centered at +108.4 p.p.m. Retention of proton coupling further split this resonance into a wide doublet of doublets. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed a doublet of doublets centered at +8.04 p.p.m. The larger of the two doublet couplings was the same as the larger doublet coupling in the proton coupled phosphorus spectrum. This coupling was indicative of a four-coordinate phosphorus. The low frequency hydride region of the proton spectrum showed a broad doublet with equally broad platinum satellites. The doublet coupling matched the smaller of the two doublet couplings in the coupled phosphorus spectrum. On the basis of these observations, the species was assigned the structure :-



δP = +39.6 p.p.m. $\quad \delta P'$ = +108.4 p.p.m.

δH = +8.04 p.p.m. $\quad {}^{1}J_{PtP}$ = 2322 Hz.

${}^{1}J_{PtP'}$ = 2426 Hz. $\quad {}^{1}J_{PtH}$ = 998 Hz.

${}^{1}J_{P'H}$ = 434 Hz. $\quad {}^{2}J_{PP'}$ = 20 Hz.

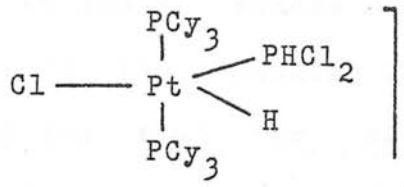
${}^{2}J_{P'H}$ = 296 Hz.

All parameters were recorded in dichlomethane at 180 K.

Warming the sample to 200 K resulted in resonances attributable to $PtH_3Cl(PCy_3)_2$[13] being observed in both the $^{31}P-\{^{1}H\}$ and the ^{1}H n.m.r. spectra. The formation of this species is in keeping with the formation of the protonated $-PCl_2$ species as both require HCl. Warming

the sample to 220 K resulted in the decomposition of this cation and the formation of a new set of resonances in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. A narrow doublet with platinum satellites was centered at +36.8 p.p.m. The coupling to platinum was fairly small for a four-coordinate platinum(II) species. In addition to these signals, a triplet with platinum satellites was centered at +141.3 p.p.m. Retention of proton coupling broadened the low frequency resonance and split the triplet into a wide doublet of quartets. The doublet coupling was indicative of a four-coordinate phosphorus. The change from a triplet to a quartet suggests that the resonance is actually an overlapping doublet of triplets where the two couplings are the same. The only likely way in which this could occur is if there was a coupling to a cis hydride. The ^{1}H nmr spectrum showed a complex hydride resonance centered at -14.8 p.p.m. Due to undissolved material in the tube, the quality of the spectrum was too poor to allow line narrowing techniques to be used to elucidate the pattern. A broad doublet with platinum satellites centered at +7.84 p.p.m. was assigned as arising from the hydrogen bound to the unique phosphorus on the basis of its chemical shift and its coupling to phosphorus matched the value obtained from the coupled phosphorus spectrum. This information suggests that the platinum is coordinated to two tricyclohexyl phosphines, one ligand containing a P-H and a hydride cis to this ligand. As the platinum coupling is too large for the species to be

six-coordinate, the structure was assigned as being



$\delta P = +36.8$ p.p.m. $\quad \delta P' = +141.3$ p.p.m.

$\delta P\underline{H} = +7.84$ p.p.m. $\quad \delta Pt\underline{H} = -14.81$ p.p.m.

$^1J_{PtP} = 2040$ Hz. $\quad ^1J_{PtP'} = 3296$ Hz.

$^1J_{PtH} = 1104$ Hz. $\quad ^1J_{P'H} = 349$ Hz.

$^2J_{PP'} = 26$ Hz. $\quad ^2J_{P'H} = 26$ Hz.

$^2J_{P'H} = 13$ Hz.

Further warming in an attempt to obtain better quality proton spectra resulted in the decomposition of this species and the formation of cis and trans $PtCl_2(PCy_3)_2$. No further new species were observed as the sample was brought to ambient temperature.

3.8. Determination of reaction stoichiometry.

Due to the presence of parallel decomposition reactions forming cis and trans $PtCl_2(PEt_3)_2$, it was difficult to determine the stoichiometry of the reaction between $PtClH(PEt_3)_2$ and PCl_3. The reaction between $PBrH(PEt_3)_2$ and PBr_3 also presented problems involving accurate measurement of the amount of PBr_3 added. The very low vapour pressure and the tendency of the compound to dissolve in the stopcock grease made accurate measurement on the vacuum line difficult. The method used was to prepare and standardise a solution of PBr_3 in CD_2Cl_2 described in chapter 2. A series of n.m.r. tubes was then prepared with different stoichiometries and the

$^{31}P-\{^{1}H\}$ n.m.r. spectra recorded after prolongued standing at 250 K. Excess PBr_3 was found to be present as soon as the combining ratio PBr_3 : Pt exceeded 1:2. This implies that the the overall reaction may represented as :-

$$PBr_3 + 2PtBrH(PEt_3)_2 \rightarrow PtBr_2(PEt_3)_2 + PtBr(PEt_3)_2(P'H_2Br_2)$$

3.9. Discussion.

The major problem arising from the reactions described in this chapter is the difficulty in accounting for the formation of the species containing a coordinated $-PH_2X_2$ group. This process must involve HX, as the rate of formation of the chloro species is increased and occurs at lower temperatures if the PCl_3 used has not been rigorously freed of HCl. This was determined in the early stages of this work before a satisfactory method had been found for removing HCl from PCl_3. However, addition of excess HCl to the $-PCl_2$ species results in the reversible protonation of the unique phosphorus between 200 and 250 K and inhibits the formation of the PH_2Cl_2 species. This implies that protonation of the $-PCl_3$ species is not involved in the transformation of $PtCl(PEt_3)_2(P'Cl_2)$ into $PtCl(PEt_3)_2(P'H_2Cl_2)$. It seems more probable that the platinum centre is involved in this process. It is possible that addition of HCl results in reversible addition to the $PtCl(PEt_3)_2(PCl_2)$ followed by elimination of PCl_2H. Rapid readdition of the PCl_2H to produce a six-coordinate species containing

a terminal -PClH group. Reductive elimination of HCl from this species is then followed by addition of this HCl across the unique phosphorus of the residual four-coordinate -PClH species to produce $PtCl(PEt_3)_2(P'H_2Cl_2)$. This proposed mechanism is illustrated in fig.3.9.

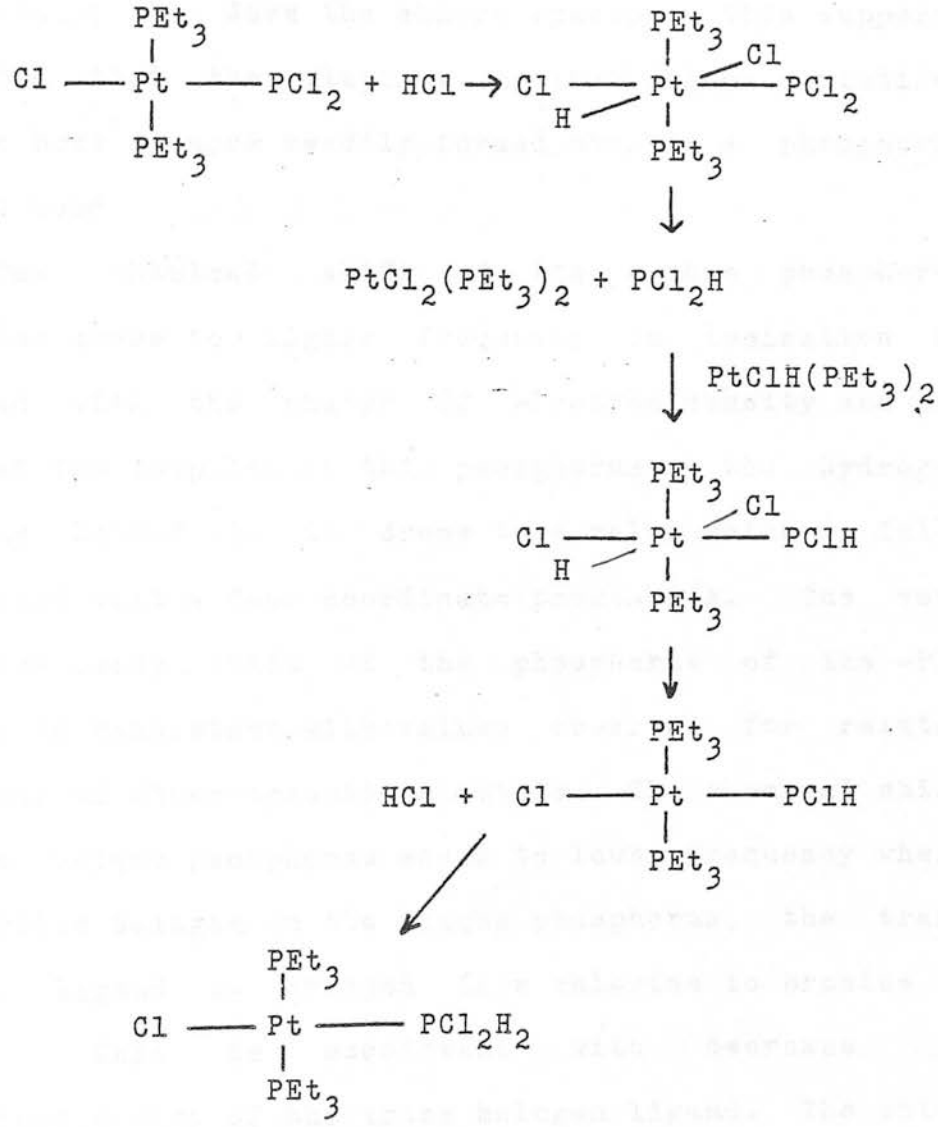


Fig.3.9 Proposed mechanism for the formation of $PtCl(PEt_3)_2(P'H_2Cl_2)$

In order for this mechanism to be acceptable, the

species containing the bound -PClH group must add HCl so rapidly that neither the bound nor the free PCl_2H can be detected. It is known that $PtCl_2H_2(PEt_3)_2$ reversibly loses HCl (although the degree of dissociation is only slight) and its presence might thus impose a close control on the concentration of free HCl in the system.

It should be noted that the bromo-species forms more readily than does the chloro species. This supports the idea that the platinum is involved as a platinum bromine bond is more readily formed than is a phosphorus bromine bond.

The chemical shift of the unique phosphorus resonance moves to higher frequency on ionisation as expected with the change of electron density and the value of the coupling of this phosphorus to the hydrogen directly bonded to it drops to a value which is fully consistent with a four coordinate phosphorus. The very high frequency shift of the phosphorus of the $-PX_2$ ligands is consistent with values observed for related compounds of other transition metals. The chemical shift of the unique phosphorus moves to lower frequency when, for a given halogen on the unique phosphorus, the trans halogen ligand is changed from chlorine to bromine to iodine. This is consistent with decrease of electronegativity of the trans halogen ligand. The shift to higher frequency as the halogen directly bound to the unique phosphorus increases in weight and the low frequency shift caused by oxidation at the platinum centre are as would be predicted.

The most surprising feature of all of the n.m.r. parameters is the values of the platinum coupling to the unique phosphorus in the species containing terminal-PX_2 groups. These values are all exceptionally small, ranging from 186 to a maximum of 465 Hz. For a platinum(II) species in which the phosphorus is also four-coordinate, the values of $^1J_{PtP}$ are almost invariably in excess of 2000 Hz. For the $P'Cl_2$ species, this coupling constant decreases as the halogen ligand trans to the unique phosphorus increases in atomic weight. As the two ligands share a common orbital, the large change observed is understandable. The coupling constant also decreases as the platinum centre is oxidised from Pt(II) to Pt(IV) in the bromo system. This decrease on oxidation is smaller than expected (186 $\longrightarrow$ 167 Hz.) which tends to imply that in these systems at least $^1J_{PtP'}$ is affected by other factors. In platinum(II) complexes with four-coordinate phosphorus trans to a halogen, the coupling, $^1J_{PtP}$ is of the order 3000 -- 4000 Hz. The compounds in this work, with the unique phosphorus trans to a halogen, show $^1J_{PtP'}$ to be of the order of 4000 $\longrightarrow$ 5000 Hz whether the unique phosphorus is formulated as being four or five coordinate. It is also worthy of note that the chemical shift of the unique phosphorus in these species is to high frequency of the corresponding bromo species. The shift from chlorine to bromine is in the same direction[14] as in PX_5 or POX_3, but in the opposite direction in PX_3 and in $PtP'X_2$. This again emphasises that the species

derived from PH_2X_2 contain phosphorus(V).

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CHAPTER 4.

REACTIONS OF $PtCl(PEt_3)_2(P'Cl_2)$ WITH NON-TRANSITION METAL SUBSTRATES.

4.1. INTRODUCTION.

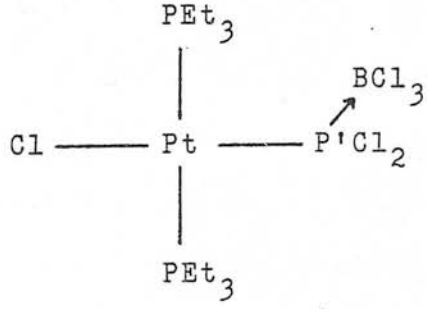
Following the preparation in this department of the species $Ir(CO)Cl_2(PEt_3)_2(PX_2)$ where X = Cl or F, wide ranging studies have been carried out on their reactions.[1,2,3,4] In both of these species, the central Ir(III) atom may be regarded as being coordinatively saturated. As such, any addition reactions are almost certain to occur at the unique phosphorus atom which is capable of undergoing either oxidative addition or donation of its lone pair to form a bond. The range of reactions observed was in both cases wide, and a variety of novel species were observed and, in some cases, isolated.

The species $PtCl(PEt_3)_2(PCl_2)$, whose preparation has been described in Chapter 3 of this work, has the potential for similar reactions at the unique phosphorus centre. Additionally, it is coordinatively unsaturated at the platinum(II) centre which gives the potential for an alternative reaction pathway. Accordingly, it was decided to undertake a study of the reactions of this species. The reactions in this chapter will be those involving non-transition metal species. The following chapter will detail reactions with transition metal substrates.

4.2.1. Reaction with Boron trichloride

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 180 K showed in

addition to the resonances associated with $PtCl(PEt_3)_2(PCl_2)$, a narrow doublet with satellites centred at +26 ppm and a broad featureless hump with satellites at ca. +136 ppm. The size of the platinum coupling to the triethyl phosphine signal at +26 ppm was indicative of a four-coordinate, platinum(II) species. Further warming to 200 K resulted in the dissapearance of the signals due to $PtCl(PEt_3)_2(PCl_2)$ and the resolving of the resonance at +136 into a broad 1:1:1:1 quartet with associated platinum satellites. (fig.4.1) The $^{11}B-\{^1H\}$ n.m.r. spectrum at this temperature showed only one signal, a doublet with associated platinum satellites centred at +7 ppm. (fig.4.2.) The doublet coupling of 143 Hz. corresponding to the quartet coupling in the phosphorus spectrum. Retention of proton coupling had no effect on the boron spectrum. These observations are consistent with the structure below.



$\delta P = +26.7$ ppm $\quad {}^1J_{PtP'} = 3780$ Hz

$\delta P' = +136.8$ ppm $\quad {}^1J_{P'B} = 136$ Hz

$\delta B = +7.0$ ppm $\quad {}^2J_{PP'} = 12$ Hz

${}^1J_{PtP} = 2192$ Hz

All parameters were recorded in dichloromethane at 200 K.

These figures are consistent with those obtained by Pilkington[4] for the BCl_3 adduct of

Fig. 4.1. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + BCl_3 at 200 K.

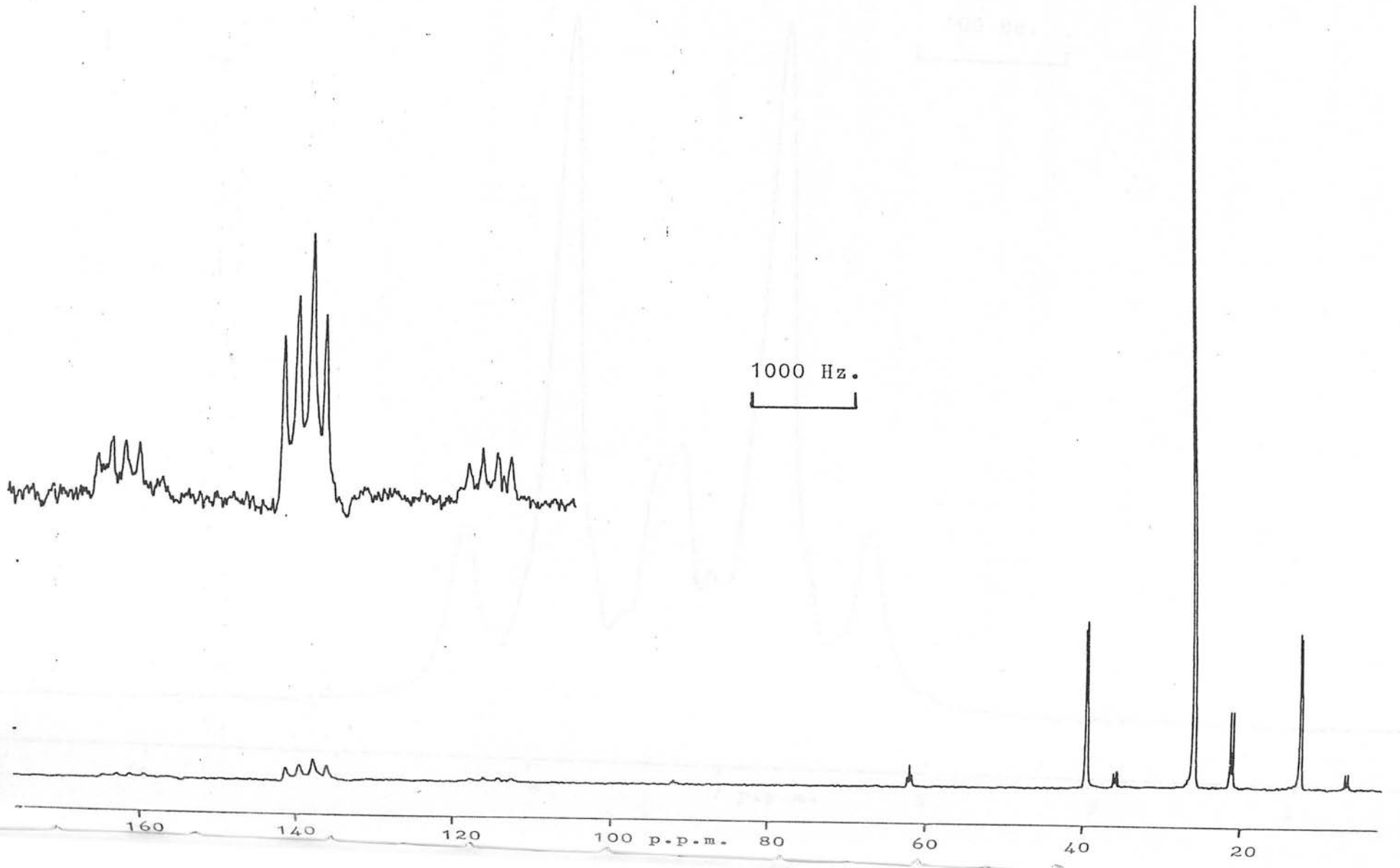
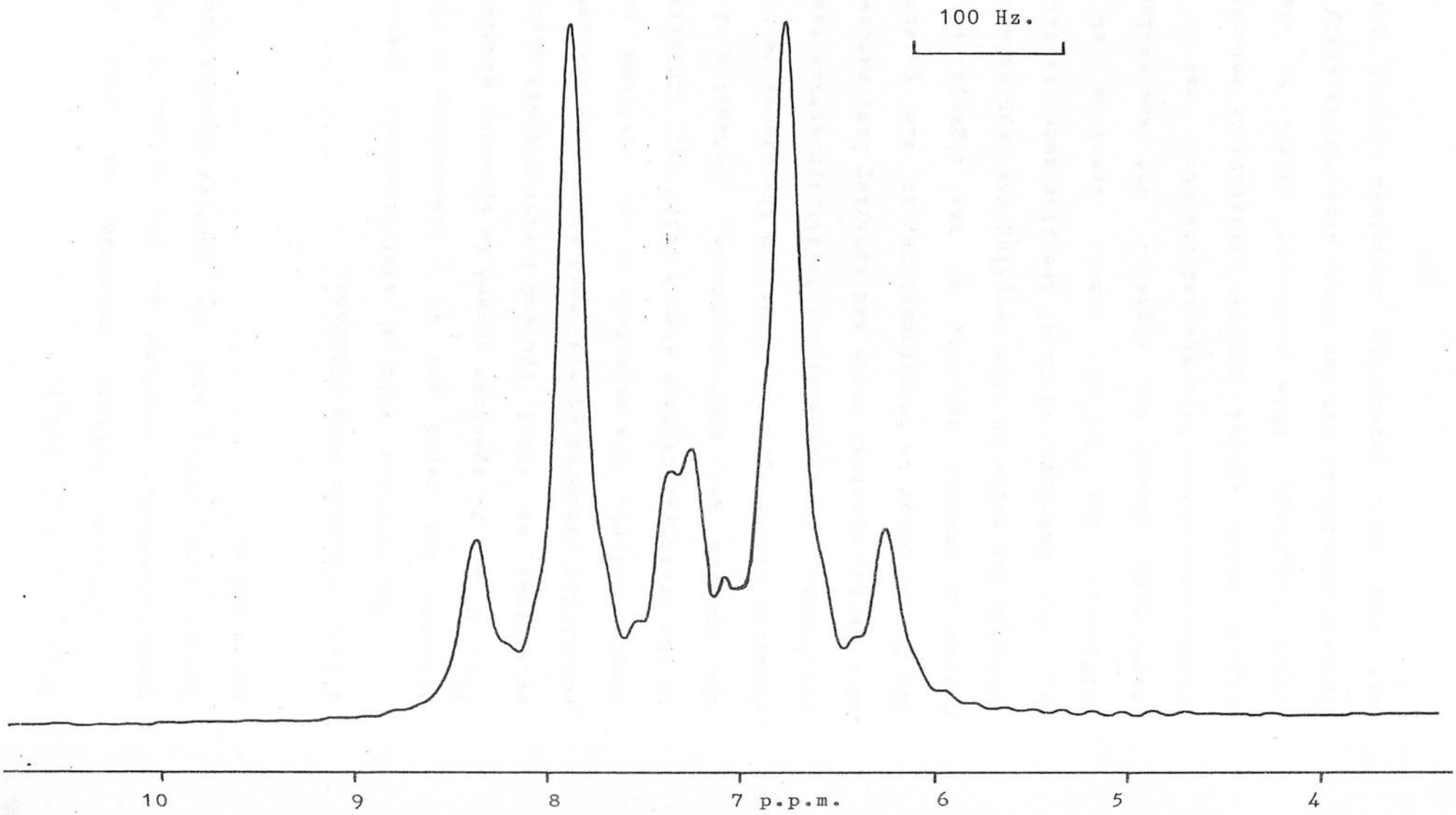


Fig. 4.2. $^{11}B-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2) + BCl_3$ at 200 K.



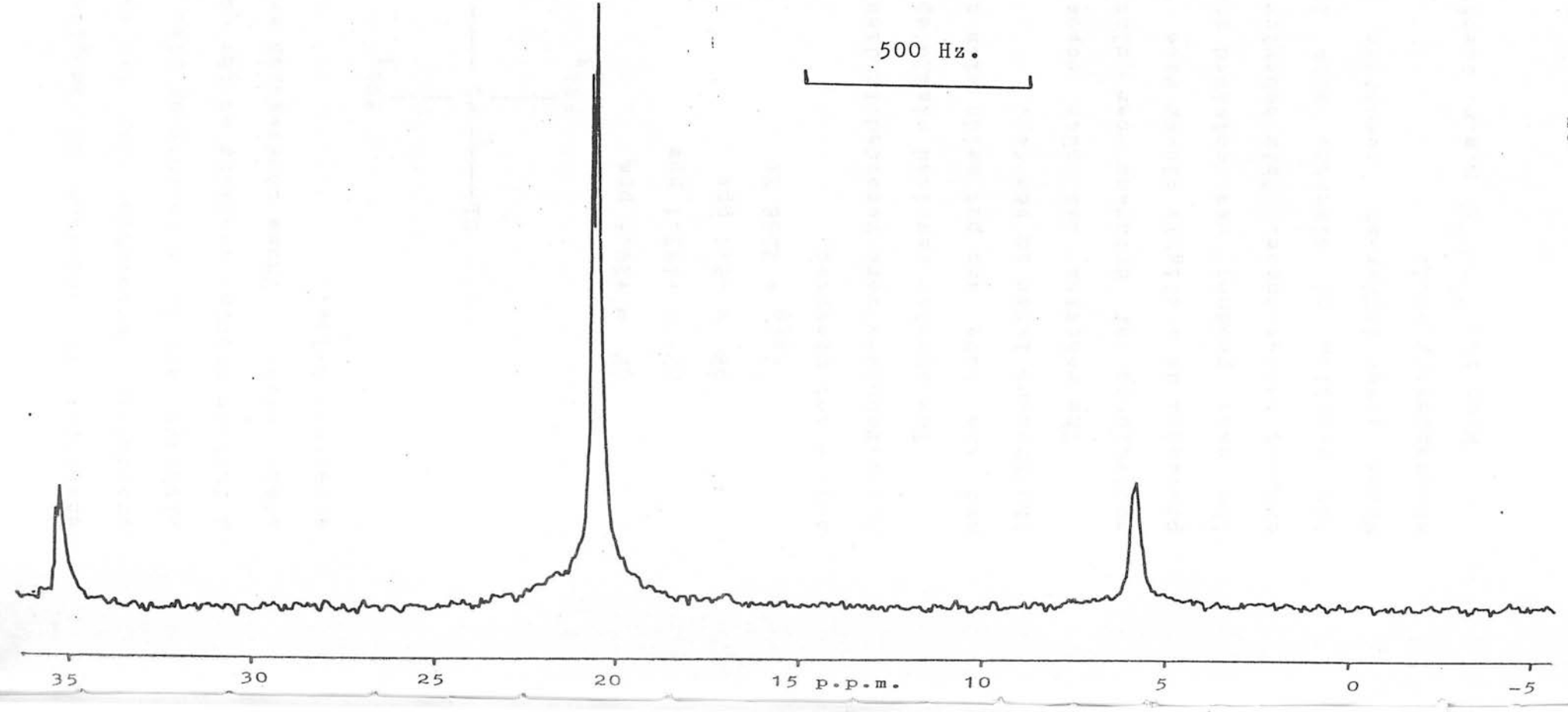
$Ir(CO)Cl_2(PEt_3)_2(PCl_2)$.

Further warming resulted in loss of the phosphorus-boron coupling as the unique P resonance became very broad and the species finally decomposed above 273 K.

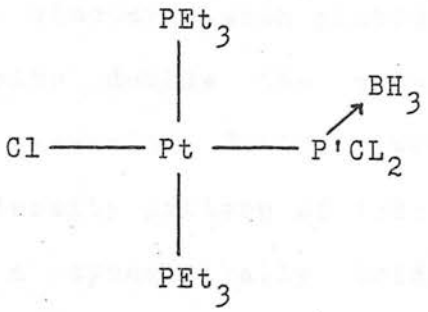
4.2.2. Reaction with Diborane.

The reaction with a stoichiometric quantity of diborane was rapid and at a temperature of 193 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed an apparent singlet with satellites at +20.5 ppm and a rather broad signal with satellites centered at +193 ppm; these were assigned to a single product. The magnitude of the platinum coupling to the triethylphosphine signal (2358 Hz.) indicated that the species was four-coordinate. Retention of proton coupling had no apparent effect on the resonance to high frequency. On observing the triethylphosphine resonance at a narrow spectral width and applying line narrowing to the F.I.D. prior to transformation, it was possible to detect a doublet coupling on the signals. (fig.4.3) Although the value of this coupling was approximately 9 Hz, the intrinsic width of the line made its detection difficult. The $^{11}B-\{^1H\}$ n.m.r. spectrum at this temperature showed two signals. One was assigned as arising from excess Diborane and the other was a broad singlet which showed quartet structure on retention of proton coupling. This resonance showed no sign of platinum satellites but the lines were sufficiently broad that they were presumably contained within the line

Fig.4.3. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + B_2H_6 at 193 K.



envelope. The absence of coupling to phosphorus is presumably accounted for by the same explanation. Although very large amounts of line narrowing did suggest a further doublet coupling on the quartet it was by no means clear. These observation are consistent with the structure below.



δP	= +20.5 ppm	$^1J_{PtP'}$	= 3011 Hz
$\delta P'$	= +193.1 ppm	$^1J_{BH}$	= 95 Hz
δB	= -8.1 ppm	$^1J_{P'B}$	= n.o.
$^1J_{PtP}$	= 2358 Hz	$^2J_{PP'}$	= 9 Hz.

n.o. = not observed.

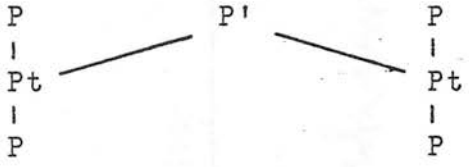
All parameters were recorded in dichloromethane at 200 K

The species remained stable up to room temperature and the tube was put aside with a view to isolation of the product later in the day.

The reaction was then repeated using 0.5 mole equivalents of diborane per platinum. The reaction proceeded at a slighly slower rate than previously but the same product was obtained and again was stable to ambient temperatures. This behavior is in contrast to the reaction of diborane with $Ir(CO)Cl_2(PEt_3)_2(PCl_2)$ which gave different reactions dependant on the stoichiometry used.

When the $^{31}P-\{^1H\}$ n.m.r. spectrum of the first tube

was rechecked prior to opening, the simple product had decomposed and a completely new species was present. The doublet at +20.5 had been replaced a doublet at +13.1 ppm and the size of the coupling to platinum indicated it to be a four-coordinate platinum (II) species. The signal arising from the unique phosphorus was now at -151.9 ppm and showed quintet stucture with platinum satellites. The satellites were also double the normal intensity. Closer examination revealed further weak satellites giving rise to an intensity pattern of 1:8:18:8:1. This is indicative of a symmetrically bridged binuclear species of the type



Retention of proton coupling split the quintet into a wide triplet of quintets with satellites (fig.4.4). The size of the triplet coupling (342 Hz.) is typical for a four-coordinate phosphorus; thus suggesting that the bridge between the two metal centres is a PH_2 group. The chemical shift of the unique P is in keepng with that of other bridging PH_2 groups.[5] The ^1H nmr spectrum showed the PH_2 resonance as a wide doublet of quintets with Platinum satellites. (fig.4.5) There was no hydride signal to low frequency , which in conjunction with the absence of any coupling from the ligand trans to the bridge suggests these ligands are probably chlorides. The structure below is consistent with these observations.

Fig. 4.4. ^{31}P n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2) + B_2H_6$ at 250 K.

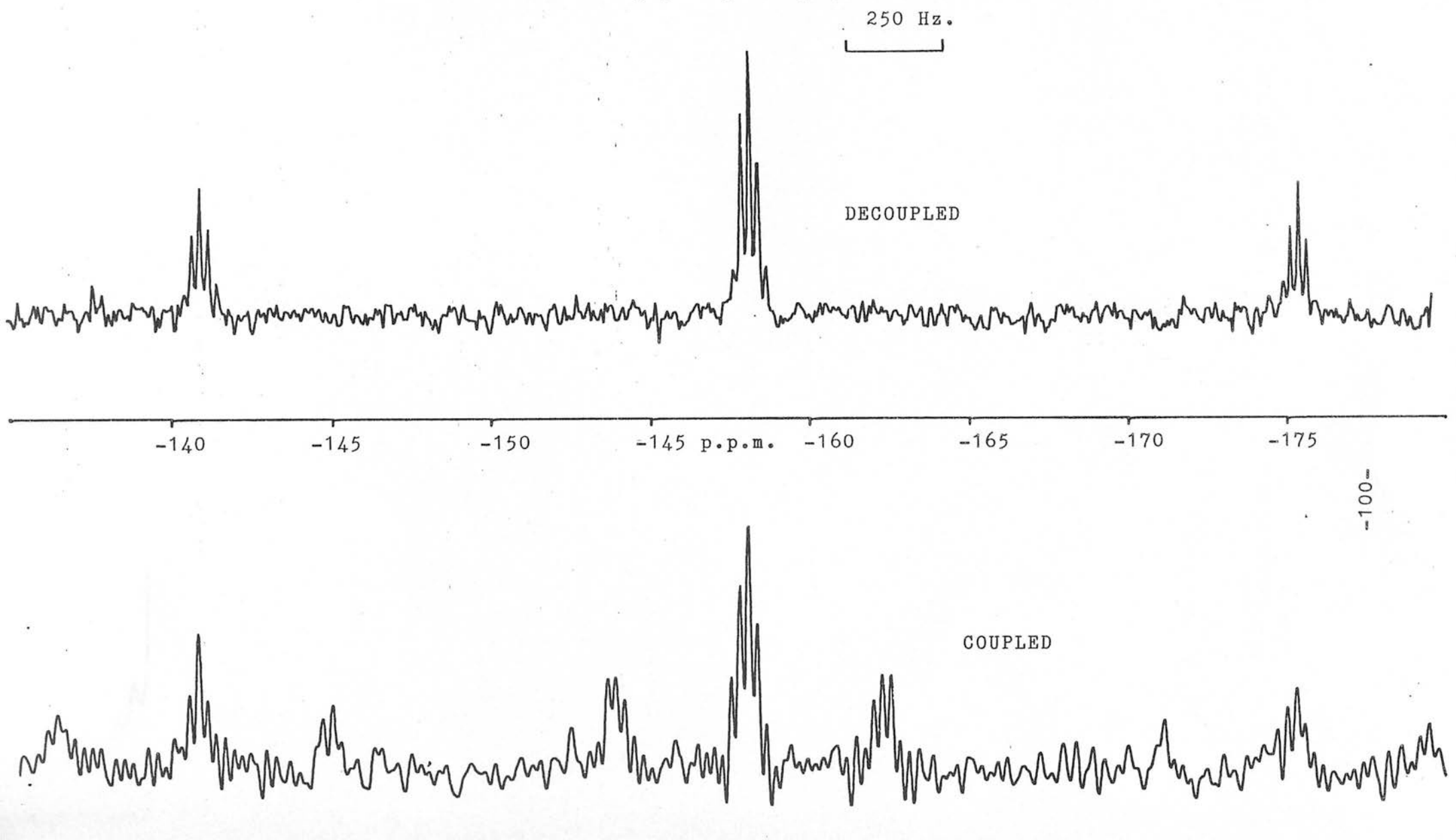
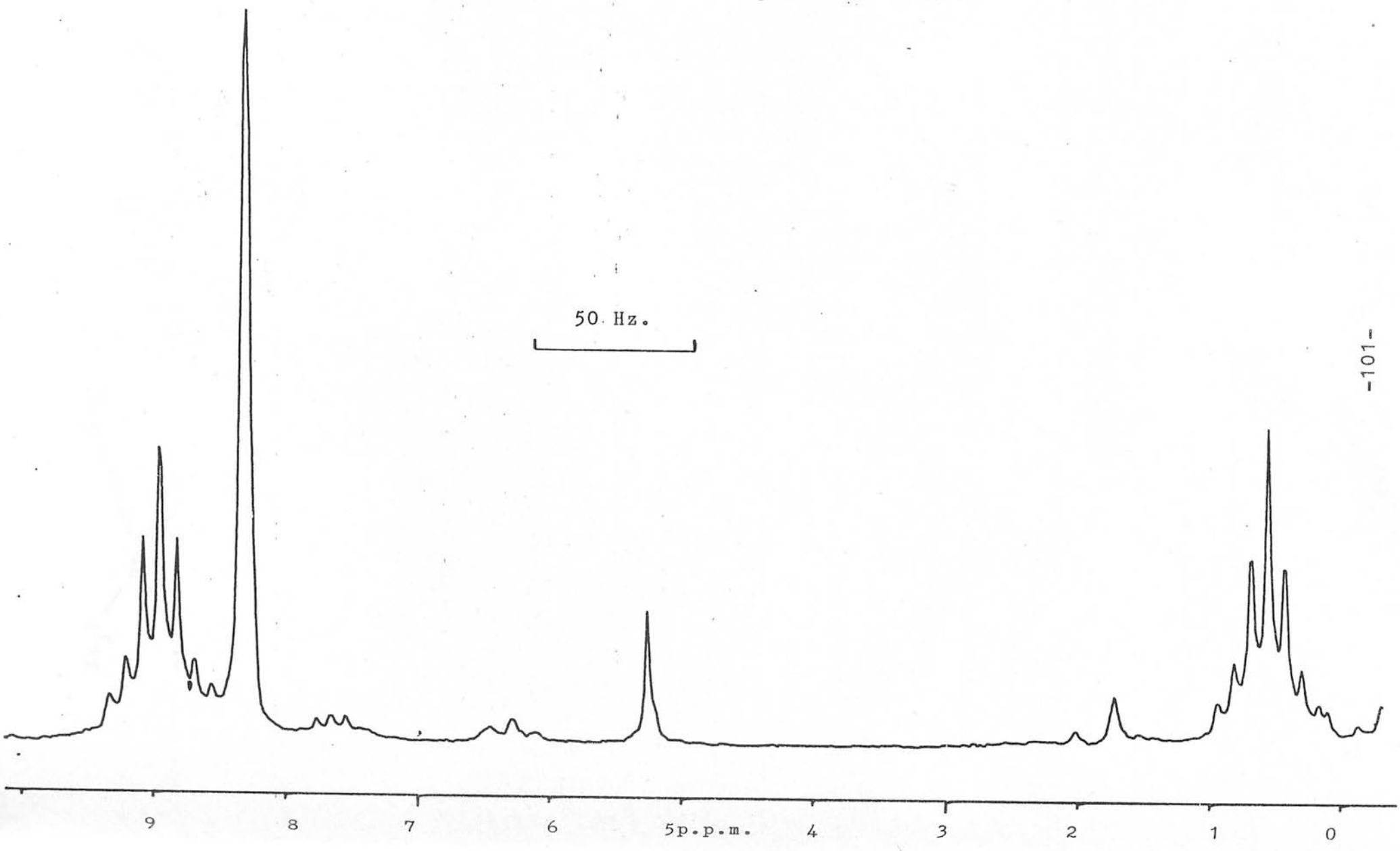
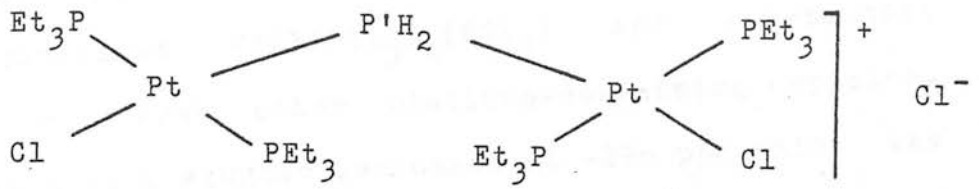


Fig. 4.5. ^{1}H n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + B_2H_6 at 250 K.





$\delta P = +13.1$ ppm $\quad {}^{1}J_{PtP'} = 2796$ Hz.

$\delta P' = -151.9$ ppm $\quad {}^{2}J_{PP'} = 22$ Hz.

${}^{1}J_{PtP} = 2266$ Hz $\quad \delta PH_2 = +4.91$ p.p.m.

${}^{1}J_{P'H} = 342$ Hz $\quad {}^{2}J_{PtH} = 19$ Hz.

All parameters were recorded in dichloromethane at 273 K

Ferrier [5] et al have synthesised analogous species with a variety of ligands rather than chloride trans to the PH_2 bridge and their parameters are consistent with the values obtained for the species above.

The identity of the species however poses a problem as to the mechanism of its formation. In an attempt to elucidate this mechanism, the reaction was repeated and monitored by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy at 273 K over a period of several hours. However no detectable intermediates were observed in the transition from simple adduct to the bridged species. Pilkington[4] studied the reaction of B_2H_6 with $Ir(CO)Cl_2(PEt_3)_2(PCl_2)$ and initially observed a simple BH_3 adduct but also detected a species which contained a BCl_3 adduct of a terminal PH_2 group. The mechanism by which this process occurs is not known but if a similar process occured in the platinum case, it is probable that the unstable terminal PH_2 group would form a bridge.

4.2.3. Reaction with Chlorine.

Reaction with a stoichiometric amount of chlorine

was rapid and at 180 K the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed unreacted $PtCl(PEt_3)_2(PCl_2)$ and substantial amounts of three other platinum-containing species. There was also a singlet resonance at -296 ppm which was assigned as arising from $[PCl_6]^-$ on the basis of its chemical shift. The three platinum containing species were identified by their standard n.m.r. parameters as being cis,cis,trans-$PtCl_2H_2(PEt_3)_2$, trans-$PtCl_4(PEt_3)_2$ and trans-$PtCl_2(PEt_3)_2$. Increasing the temperature to 210 K resulted in the loss of signals attributable to $PtCl(PEt_3)_2(PCl_2)$ and the formation of cis - $PtCl_2(PEt_3)_2$ in addition to the other species. It was apparent that the main reaction had occured at the platinum centre rather than the unique phosphorus. Presumably some reaction had occured at the phosphorus centre as testified to by the formation of $[PCl_6]^-$. Carrying out the reaction with a two-fold excess of chlorine resulted in the rapid and exclusive formation of a mixture of $[PCl_6]^-$ and trans-$PtCl_4(PEt_3)_2$ at 180 K. Using a two-fold excess of $PtCl(PEt_3)_2(PCl_2)$ gave the same products as the stoichiometric reaction but in slightly different ratios.

4.2.4. Reactions with Hydrogen

The formation of the species $ClPt(PEt_3)_2(PH_2Cl_2)$ has been discussed in detail in Chapter 3 of this work. It appeared that the unique phosphorus of $PtCl(PEt_3)_2(PCl_2)$ was hydrogenated in some manner by $PtCl_2H_2(PEt_3)_2$. The mechanism by which this reaction proceeds is difficult to envisage other than allowing for

the reductive elimination of hydrogen by $PtCl_2H_2(PEt_3)_2$ and the subsequent reduction of the unique phosphorus of $PtCl(PEt_3)_2(PCl_2)$. Accordingly it was decided to attempt the hydrogenation by other means in the hope of producing a clean sample of $ClPt(PEt_3)_2(PH_2Cl_2)$ with a view to isolation attempts.

A sample of $PtCl(PEt_3)_2(PCl_2)$ in CD_2Cl_2 was prepared by the normal methods and held at a temperature of 227 K while hydrogen was slowly bubbled through the solution, initially under an atmosphere of dry nitrogen. After one hour the solution was transferred to a n.m.r. tube, cooled to 77 K and sealed under vacuum. The $^{31}P-\{^1H\}$ n.m.r. spectrum revealed that absolutely no reaction had taken place. The entire procedure was then repeated at a temperatures of 240 K and 260 K with the same end result. In the mechanism proposed above for the hydrogenation, it seems that reductive elimination of hydrogen from $PtCl_2H_2(PEt_3)_2$ results in the presence of $PtClH(PEt_3)_2$ in the reaction mixture. Accordingly, a small amount of $PtClH(PEt_3)_2$ was added to a sample of $PtCl(PEt_3)_2(PCl_2)$ prior to bubbling hydrogen through the solution held at 240 K. Yet again $^{31}P-\{^1H\}$ n.m.r. spectrum showed no reaction to have occured. It was decided that the actual mechanism of hydrogenation was more complex than the simplistic mechanism proposed above and to abandon attempts to mimic the reaction. Instead it was decided to try an alternative route to produce $ClPt(PEt_3)_2(PH_2Cl_2)$.

It is known that many hydrogenation reactions

proceed in the presence of a catalyst, so it was decided to try the reaction with hydrogen in the presence of a catalytic amount of Wilkinson's catalyst [$Rh(PPh_3)_3Cl$]. The reaction was carried out in a Schlenk tube as above in the presence of approximately 5% of Wilkinson's catalyst. After only one minute of bubbling hydrogen through the mixture, a yellow-orange precipitate formed and the $^{31}P-\{^1H\}$ n.m.r. spectrum showed the $PtCl(PEt_3)_2(PCl_2)$ to have decomposed to the usual mixture of cis and trans $PtCl_2(PEt_3)_2$. The precipitate was insoluble in all common solvents and was assumed to be a polymeric PCl species. The reaction was repeated at lower temperatures and for shorter periods of time with the same result. Adding small amounts of Wilkinson's catalyst to $PtCl(PEt_3)_2(PCl_2)$ failed to show any reaction. It is apparent that some sort of reaction with hydrogen occurs in the presence of this catalyst but that the decomposition is very rapid. Ideally, the reaction should be studied from low temperature by n.m.r. spectroscopy but it is not possible to seal an n.m.r. tube with hydrogen present. It was decided that the problems involved with this reaction were too great to justify any further work.

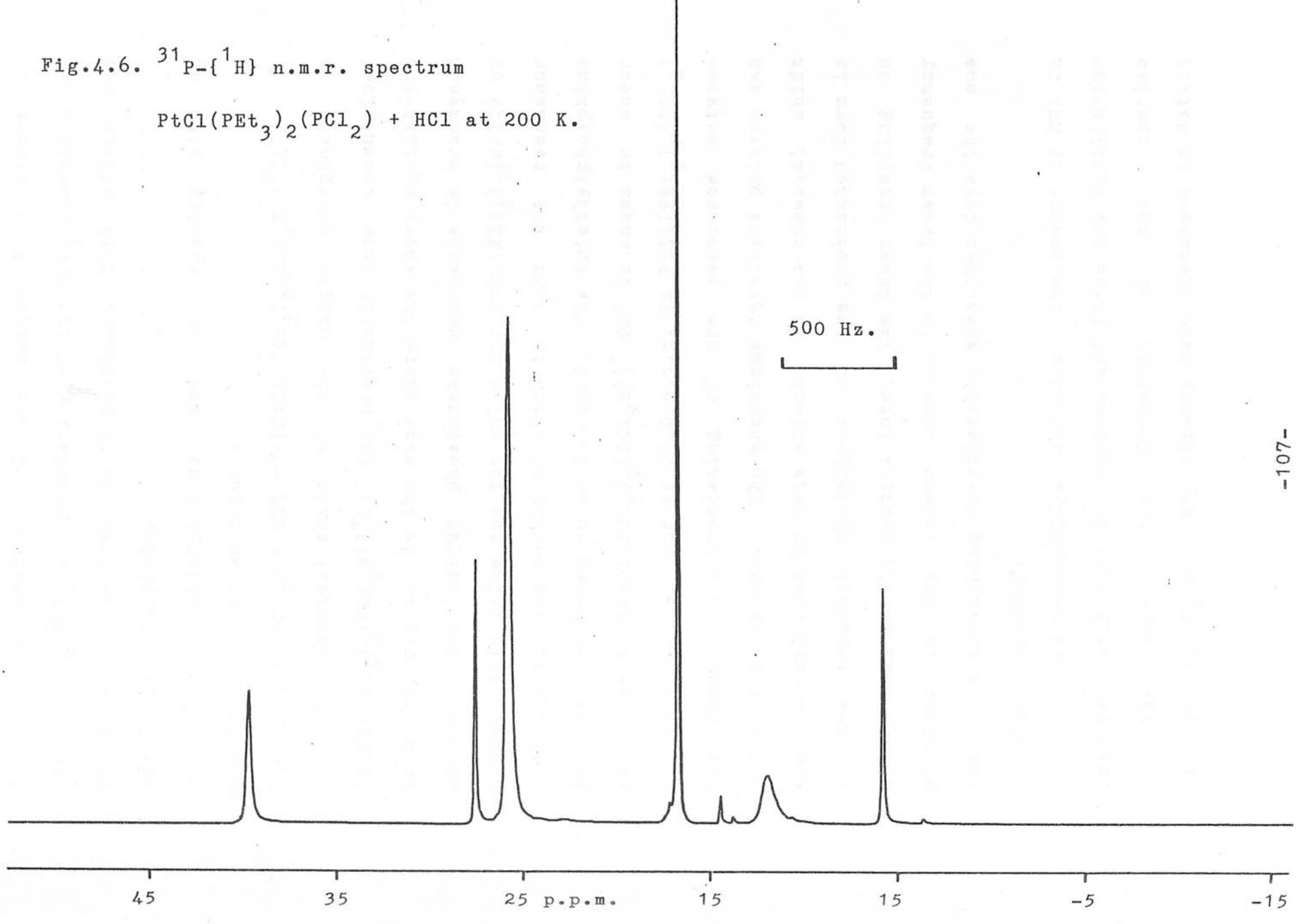
4.2.5. Reaction with Hydrogen chloride.

From the results described in Chapter 3, it was expected that this reaction would result in a simple protonation of the lone pair on the unique phosphorus.

Observing the $^{31}P-\{^{1}H\}$ n.m.r. spectrum as the solvent melted at circa 176 K revealed resonances attributable to unreacted $PtCl(PEt_3)_2(PCl_2)$, $PtClH(PEt_3)_2$ and $PtCl_2H_2(PEt_3)_2$. In addition there was a very broad resonance with satellites in the triethylphosphine region. The lower frequency satellite appeared to be less intense but broader than the one to high frequency. Raising the temperature to 180 K resulted in the loss of the resonances associated with $PtCl(PEt_3)_2(PCl_2)$ and $PtClH(PEt_3)_2$ and the formation of a small amount of PCl_3. The anomalous satellite pattern was still present (fig.4.6). Increasing the temperature resulted in a gradual sharpening of the lines and in a linear increase in the value of the coupling to platinum. At 210 K the proton coupled ^{31}P spectrum revealed a very broad hump ($W_{1/2}$ = 2500 Hz) centered at about 210 p.p.m. At this temperature, the PEt_3 resonance started to show a small doublet coupling. Increasing the temperature still further resulted in the hump moving to higher frequency and gradually sharpening. In parallel with this, the PEt_3 resonance continued to show an increased coupling to platinum and the doublet coupling became quite distinct. By 250 K the high frequency resonance had moved to +290 p.p.m. and was much sharper ($W_{1/2}$=250 Hz.). Resonances previously assigned to $ClPt(PEt_3)_2(PH_2Cl_2)$ were also detected. Raising the temperature to 273 K resulted in a spectrum which showed $PtCl(PEt_3)_2(PCl_2)$, $PtCl_2H_2(PEt_3)_2$ and $ClPt(PEt_3)_2(PH_2Cl_2)$. All the n.m.r. parameters were normal for these species. Recooling the tube and

Fig.4.6. $^{31}P-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2)$ + HCl at 200 K.



recording the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 223 K resulted in the dissapearance of the unique P resonance of $PtCl(PEt_3)_2(PCl_2)$, broadening of its PEt_3 resonance and reduction in its coupling to platinum. This effect was compltely reversible.

These observations are in keeping with an equilibrium as shown below :-

$$PtCl(PEt_3)_2(PCl_2) + HCl \rightarrow [PtCl(PEt_3)_2(PCl_2H)]^+Cl^-$$

The chemical shift of the unique phosphorus in $[PtCl(PEt_3)_2(PCl_2H)]^+Cl^-$ has previously been ascertained to be +65 p.p.m. In the case where the above equilibrium exists, the unique phosphorus resonance is broadened between this value and the value for $PtCl(PEt_3)_2(PCl_2)$ of +312 p.p.m. The result of which is that the resonance becomes too broad to be detected. The triethylphosphine resonance in $[PtCl(PEt_3)_2(PCl_2H)]^+ Cl^-$ is known to occur at 23.7 p.p.m. and at 21.0 p.p.m. in $PtCl(PEt_3)_2(PCl_2)$ This results in a broadening of the resonance between these two values. The anomalous satellite pattern can also be explained by this effect. As the chemical shift of the triethyl phosphines of the protonated form is higher than in the neutral form, the lower coupling to platinum in the former results in the lower frequency satellite broadening considerably more than does the one to high frequency.

As the temperature increases, the amount of HCl in solution will tend to decrease and force the equilibrium to the left. The formation of the species $ClPt(PEt_3)_2(PH_2Cl_2)$ has already been discussed in detail

in Chapter 3. As the amount of HCl in solution appears to affect the position of the equilibrium, it was decided to study the reaction using an excess of HCl.

As the mixture melted, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed small amounts of the protonated species forming. By 220 K, all the resonances associated with $PtCl(PEt_3)_2(PCl_2)$ had disappeared, leaving only resonances attributable to $PtCl_2H_2(PEt_3)_2$ and $[PtCl(PEt_3)_2(PCl_2H)]^+ Cl^-$. The resonance attributable to the unique phosphorus in the latter was rather broad ($W_{1/2}$ = 50 Hz.) but sharpened to its normal line widths on recooling to 180 K. (fig.4.7.) Observing the $^{31}P-\{^{1}H\}$ n.m.r. spectrum as the reaction was warmed to ambient temperature showed no further reaction. After a period at room temperature, both the species present began to decompose, eventually leaving a mixture of cis and trans $PtCl_2(PEt_3)_2$. Although the n.m.r. parameters for the protonated species are detailed in Chapter 3, they are listed below for the sake of completeness.

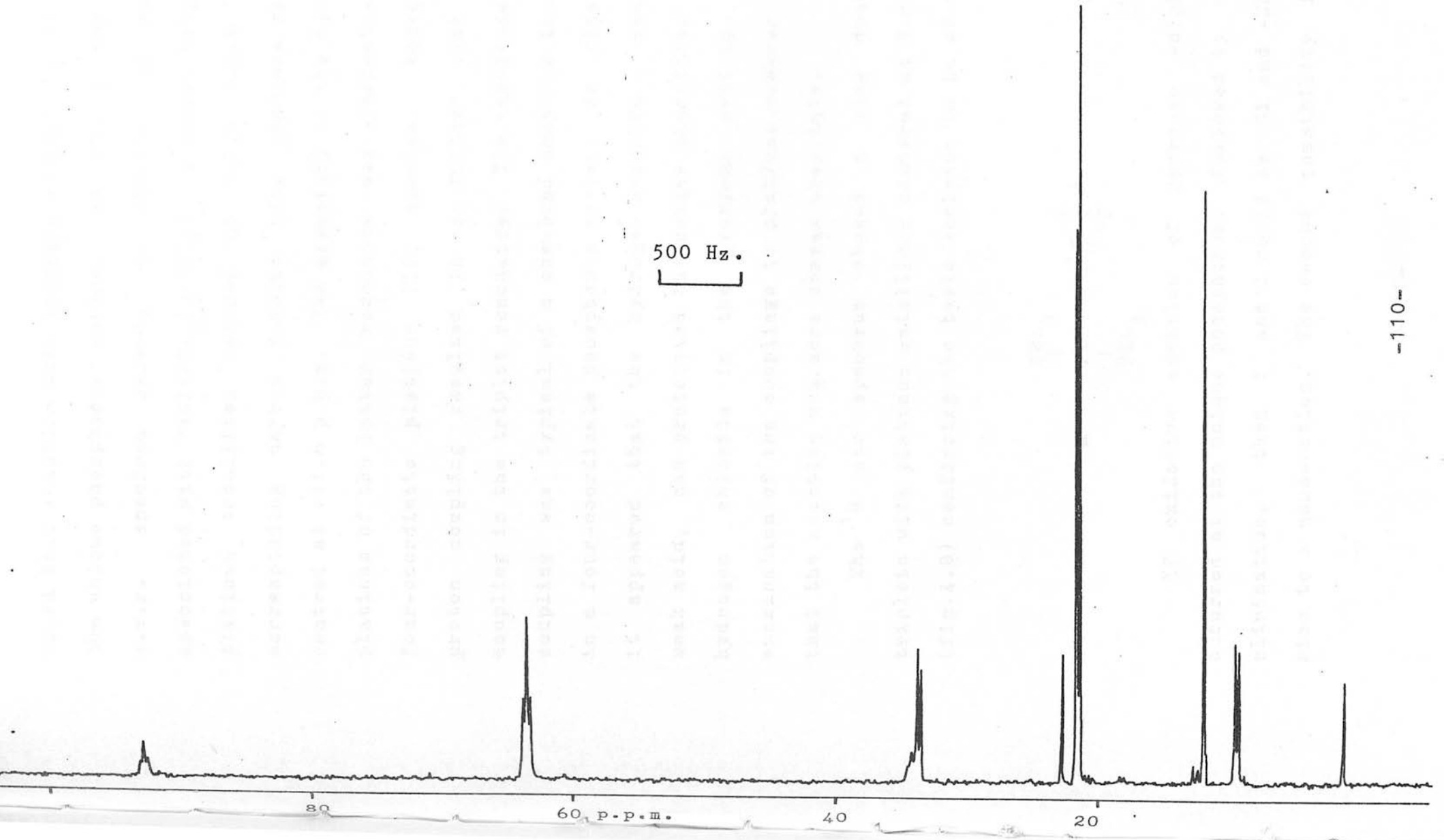
δP = +23.63 p.p.m.	$^{1}J_{P'H}$ = 550 Hz.
$\delta P'$ = +65.49 p.p.m.	$^{2}J_{PtH}$ = 235 Hz.
$\delta \underline{P}H$ = +8.69 p.p.m.	$^{2}J_{PP'}$ = 22 Hz.
$^{1}J_{PtP}$ = 1953 Hz.	$^{3}J_{HP}$ = 9 Hz.
$^{1}J_{PtP'}$ = 4740 Hz.	

All parameters were recorded in dichloromethane at 180 K.

4.2.6. Reaction with Hydrogen Sulphide

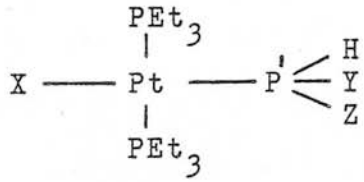
Previous workers[6] have noted that platinum-thiol complexes are generally difficult to prepare and it was

Fig. 4.7. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + HCl at 180 K.



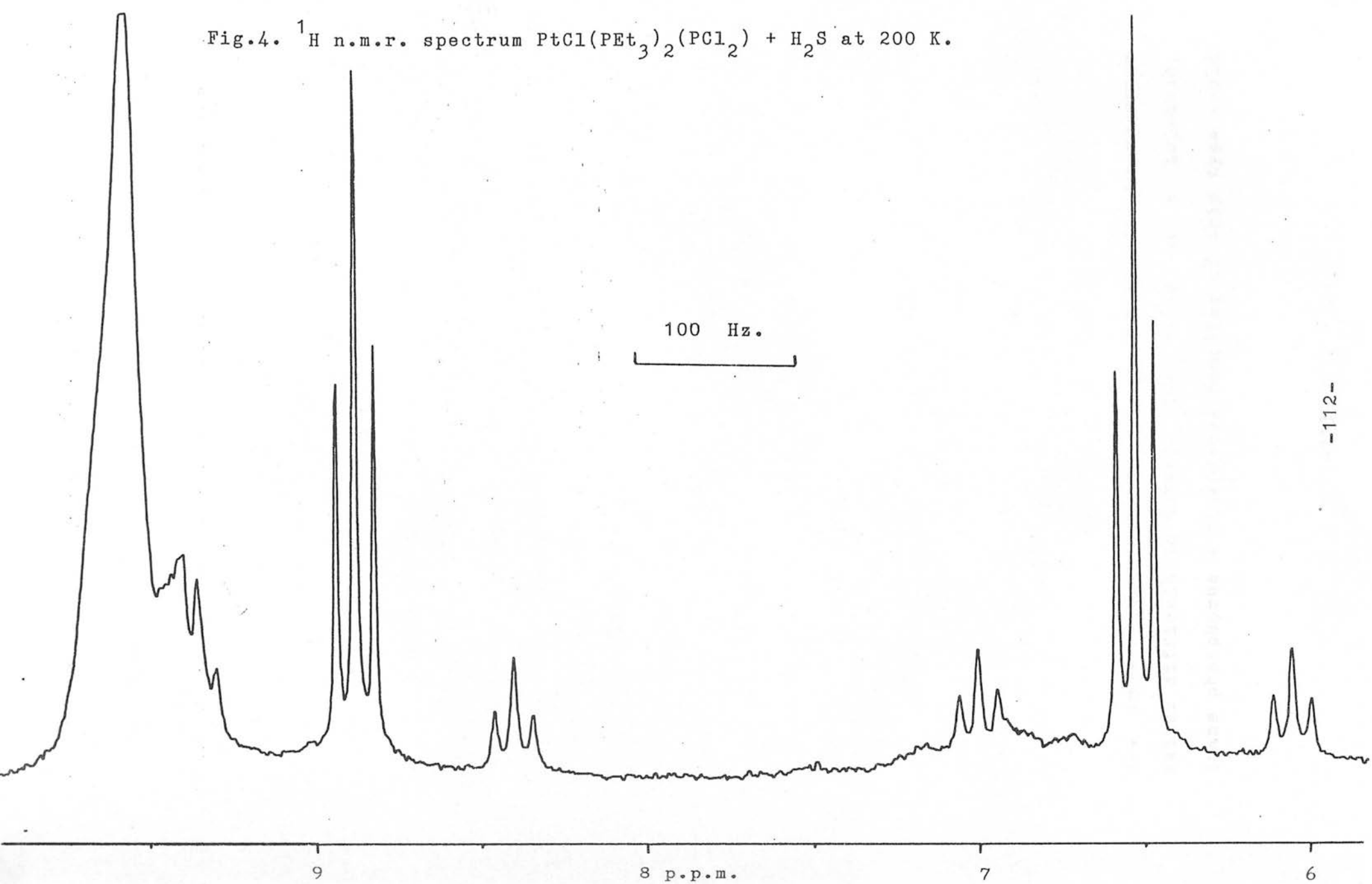
hoped that reaction with hydrogen sulphide would occur at the unique phosphorus centre. At 200 K the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed, in addition to resonances associated with $PtCl(PEt_3)_2(PCl_2)$, a narrow triplet with platinum satellites centred at +44.6 p.p.m. and a corresponding narrow doublet with platinum satellites centred at +11.6 p.p.m. The magnitude of the coupling to platinum of the latter resonance was indicative of a four-coordinate platinum (II) species. Retention of proton coupling resulted in a further wide doublet coupling in the triplet resonance. The magnitude of this coupling was typical of a one-bond coupling to a proton in a four-coordinate phosphorus system. At first sight it appeared that the hydrogen sulphide, acting as a weak acid, had protonated the unique phosphorus as did hydrogen chloride in the previous section. Closer examination of the couplings to platinum however revealed that the reaction was more compex than this.

The ^{1}H nmr spectrum showed a wide doublet of triplets with platinum satellites centered at 7.87 p.p.m. (fig.4.8) confirming the basic skeleton to be of the type

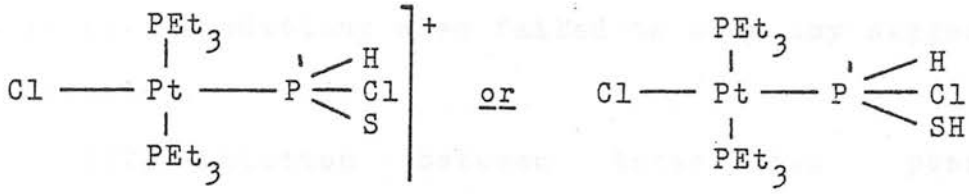


If oxidative addition of hydrogen sulphide had occurred at the unique phosphorus, followed by chloride elimination, then Y and Z could be -Cl and -SH giving rise to a mono-cation. The second possibility is that

Fig.4. ^{1}H n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + H_2S at 200 K.



this unit could deprotonate at the -SH group to leave a neutral species. It seems reasonable to assume that ligand X remains unchanged as chloride in both structures.



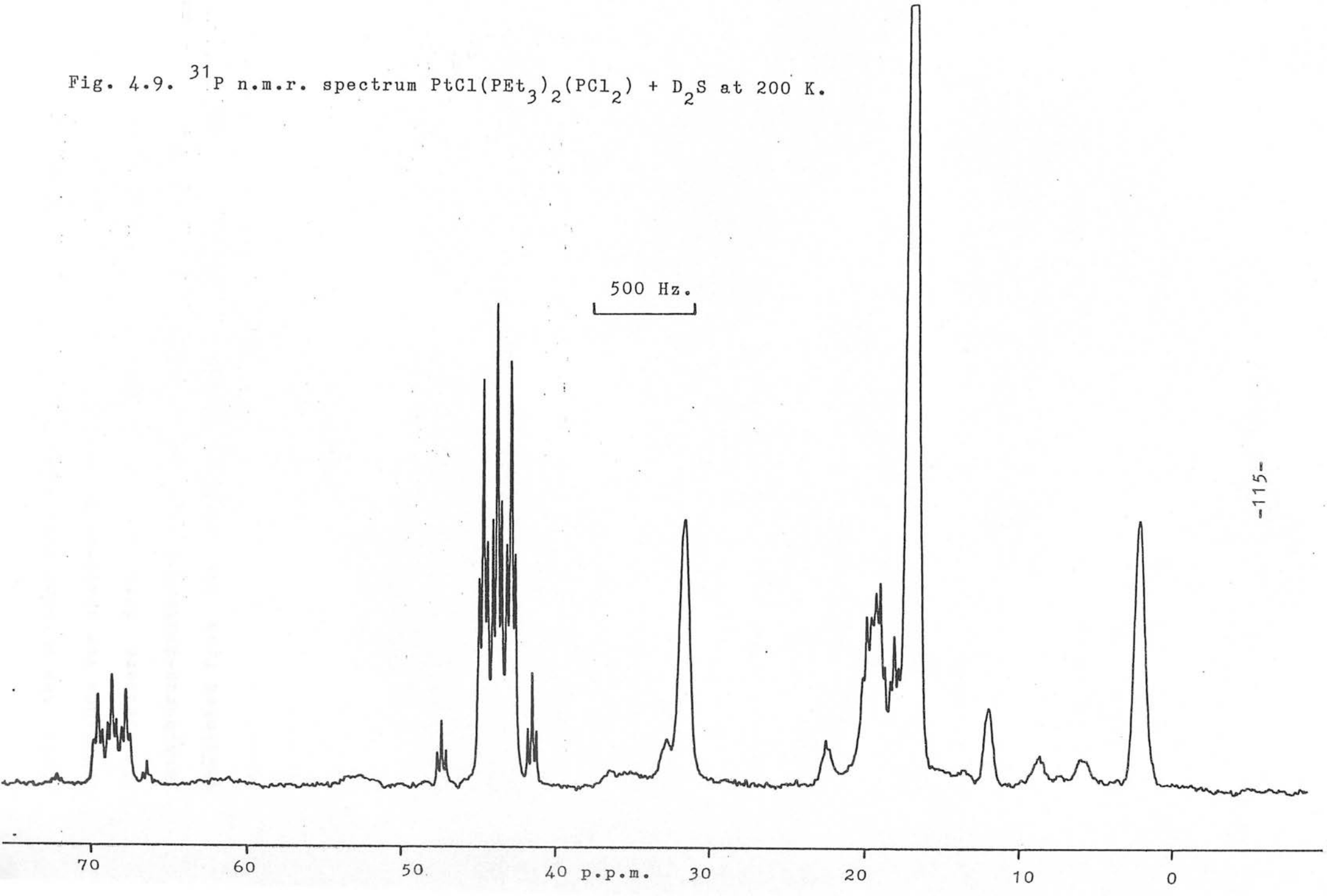
In both of these structures, however, the unique phosphorus is a chiral centre. The consequence is that the triethyl phosphines become both chemically and magnetically inequivalent. This should result in their $^{31}P-\{^{1}H\}$ n.m.r. spectrum manifesting itself as a second order ABX pattern; the X component arising from coupling to the unique phosphorus. The observed spectrum however appears to be first order. It is possible to rationalise this pattern by accepting that the spectrum is indeed second order but that the chemical shifts of the two different triethylphosphine phosphorus atoms are, by coincidence, the same. Also, the chirality relies on all the groups attached to the unique phosphorus atom being distinct. The difference between a sulphur and a chlorine is fairly small, which could result in the difference between the two triethyl phosphine groups being very small. In such a case the outer lines of the ABX pattern could well be very weak and consequently rather difficult to detect. The value of a two-bond, trans phosphorus - phosphorus coupling of this type would

probably be of the order of 400 Hz. Close examination of the spectrum failed to reveal any lines which could be attributed to these weak lines although there were other resonances in this region which may have obscured them. Examination of the central resonance under higher resolution conditions also failed to show any suggestion of splitting.

Differentiation between these two possible structures is difficult on the basis of the available information. The failure to detect a proton resonance attributable to an -SH cannot be regarded as significant as such a resonance would almost certainly lie underneath the envelope of the triethyl phosphine signals. One way to overcome this problem is to study the reaction of $PtCl(PEt_3)_2(PCl_2)$ with D_2S and then observe the ^2D n.m.r. spectrum. Any -SD resonance should be visible as there will be no signals obscuring it. Accordingly the reaction was repeated using D_2S.

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 200 K was similar to that observed with H_2S, except that the resonance associated with the unique phosphorus was now a 1:1:1 triplet of triplets with platinum satellites, the 1:1:1 triplet coupling arising from coupling to deuterium which has a spin I = 1. Retention of proton coupling had no affect on this resonance but a small triplet appeared on either side of the main resonance (fig.4.9). This was assigned as arising from a small amount of the proton form of the molecule arising from reaction with either HDS or H_2S impurities known to be present in the D_2S.

Fig. 4.9. ^{31}P n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + D_2S at 200 K.



While the protons were decoupled, its unique phosphorus resonance was obscured by the more abundant resonance of the deutero form of the product. The value of the phosphorus-deuterium coupling was very close to the value predicted from the phosphorus-proton coupling, these couplings being in the ratio of the frequencies required for resonance of the respective nuclei. i.e.

$$J_{PD} = J_{PH} \times \frac{30.722}{200.130}$$

The chemical shift of the deuterium signal was almost identical to the shift of the corresponding proton signal. Unlike the proton case, it did not prove possible to resolve any fine structure on the deuterium resonances or to evaluate the coupling to platinum. Several factors contribute to this observation. Because the experiment cannot be carried out in a deutero solvent, the instrument cannot be shimmed on the sample. For the same reason, the instrument is operating in an unlocked mode which results in a slight drift of the magnetic field during the course of the experiment. Finally, since deuterium is a quadropolar nucleus (I=1), the resonances would be expected to be rather broader than the corresponding proton signals. Resonances from quadropolar nuclei generally broaden at lower temperatures, and as the the experiment was carried out at 200 K this would also prove detrimental. The values of the couplings observed in the proton case would also be reduced by a factor of 0.1535 as mentioned above. Combined with the broadening produced by the

aforementioned factors, it is scarcely surprising that no further couplings can be detected in the deuterium spectrum.

The failure to detect a resonance which could be attributed to a -SD group strongly favours the neutral species postulated earlier. The compound remained stable to 273 K, above which temperature it decomposed to a mixture of cis and trans $PtCl_2(PEt_3)_2$ and a solid yellow residue which proved insoluble in all common solvents and was presumed to be of a polymeric nature. An impure sample of the product was isolated as a sticky yellow material at 253 K by removal of the solvent. Attempts to obtain a FAB mass spectrum met with failure as the material appeared to react with the glycerol support medium used. The n.m.r. parameters of the product are detailed below.

$\delta P = +11.90$ p.p.m. $\quad \delta P' = +44.3$ p.p.m.

$\delta H = +7.87$ p.p.m. $\quad {}^1J_{PtP} = 2382$ Hz.

${}^1J_{PtP'} = 4010$ Hz. $\quad {}^1J_{P'H} = 469$ Hz.

${}^2J_{PtH} = 190$ Hz. $\quad {}^2J_{PP'} = 22$ Hz.

${}^3J_{PH} = 11$ Hz.

Additional parameters for the deutero species are :-

$\delta D = +7.78$ p.p.m. $\quad {}^1J_{PD} = 70$ Hz.

All parameters were recorded in dichloromethane at 200 K.

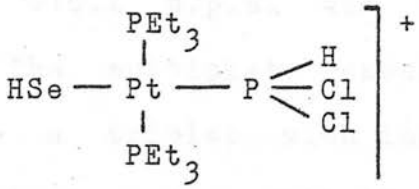
4.2.7. Reaction with Hydrogen Selenide.

In view of the questions posed by the reactions with H_2S, discussed in the previous section, it seemed logical to study the reaction with H_2Se. Previous

workers [7,8,9] have noted that selenol compounds of platinum appear to be easier to prepare than the corresponding thiol species. This gives rise to the possibility that reaction may proceed by a different mechanism to that followed in the H_2S reaction and may produce other products. The attraction of using H_2Se is that selenium posesses 7.6% ^{77}Se with I = $^1/_2$ which will manifest itself as selenium satellites in the ^{31}P and ^1H n.m.r. spectra. There is also the possibility of direct observation of the ^{77}Se n.m.r. spectrum.

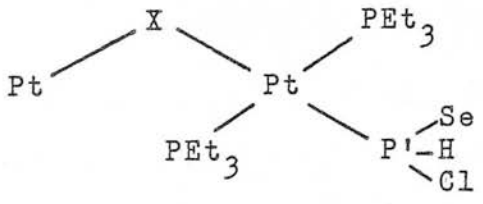
Reaction was rapid and as soon as the solvent had melted the $^{31}P-\{^1H\}$ n.m.r. spectrum showed four platinum-containig species in addition to $PtCl(PEt_3)_2(PCl_2)$ starting material. Three of these were identified by their n.m.r. parameters as being cis and trans $PtCl_2(PEt_3)_2$ and $PtCl_2H_2(PEt_3)_2$. (It was assumed that the six-coordinate species had been produced during the preparation of the $PtCl(PEt_3)_2(PCl_2)$ as there appeared to be no HCl impurity in the H_2Se.) A singlet without platinum satellites was identified as arising from $HPEt_3^+$. Additionally, there was a narrow triplet with platinum satellites centred at + 17.27 p.p.m. and a corresponding narrow doublet with platinum satellites centred at +15.80 p.p.m. The magnitude of the platinum coupling to the doublet resonance was indicative of a four-coordinate platinum (II) species. Retention of proton coupling further split the narrow triplet resonance into a wide doublet. The doublet coupling of 475 Hz was indicative of four-coordinate phosphorus. The

triplet signal arising from the unique phosphorus showed no ^{77}Se satellites suggesting that the other two ligands on this phosphorus were still chlorines. This means that the ligand trans to the unique phosphorus can no longer be chlorine as this species has already been characterised as the product from the reaction between $PtCl(PEt_3)_2(PCl_2)$ and HCl. It seems most likely that the trans ligand is a -SeH giving the structure shown below.



The chemical shift of the unique phosphorus is quite different to that in the cation with a trans chlorine ligand. This is consistent with the observation that the chemical shifts of hydrides trans to selenol groups resonate at about -10 p.p.m.compared with values between -18 and -20 p.p.m. when trans to a chloride. This is rationalised by the different trans influences of the two groups. Considering that the proton chemical shift range is very small compared with that of phosphorus, the change of 48 p.p.m. in the shift of the unique phosphorus does not appear to be unreasonable. It is not simple to postulate a mechanism for the formation of this molecule other than to suggest that the initial oxidative addition occured at the platinum centre followed by a rapid intermolecular rearrangement resulting in the transfer of the hydrogen to the unique phosphorus and elimination of the chloride.

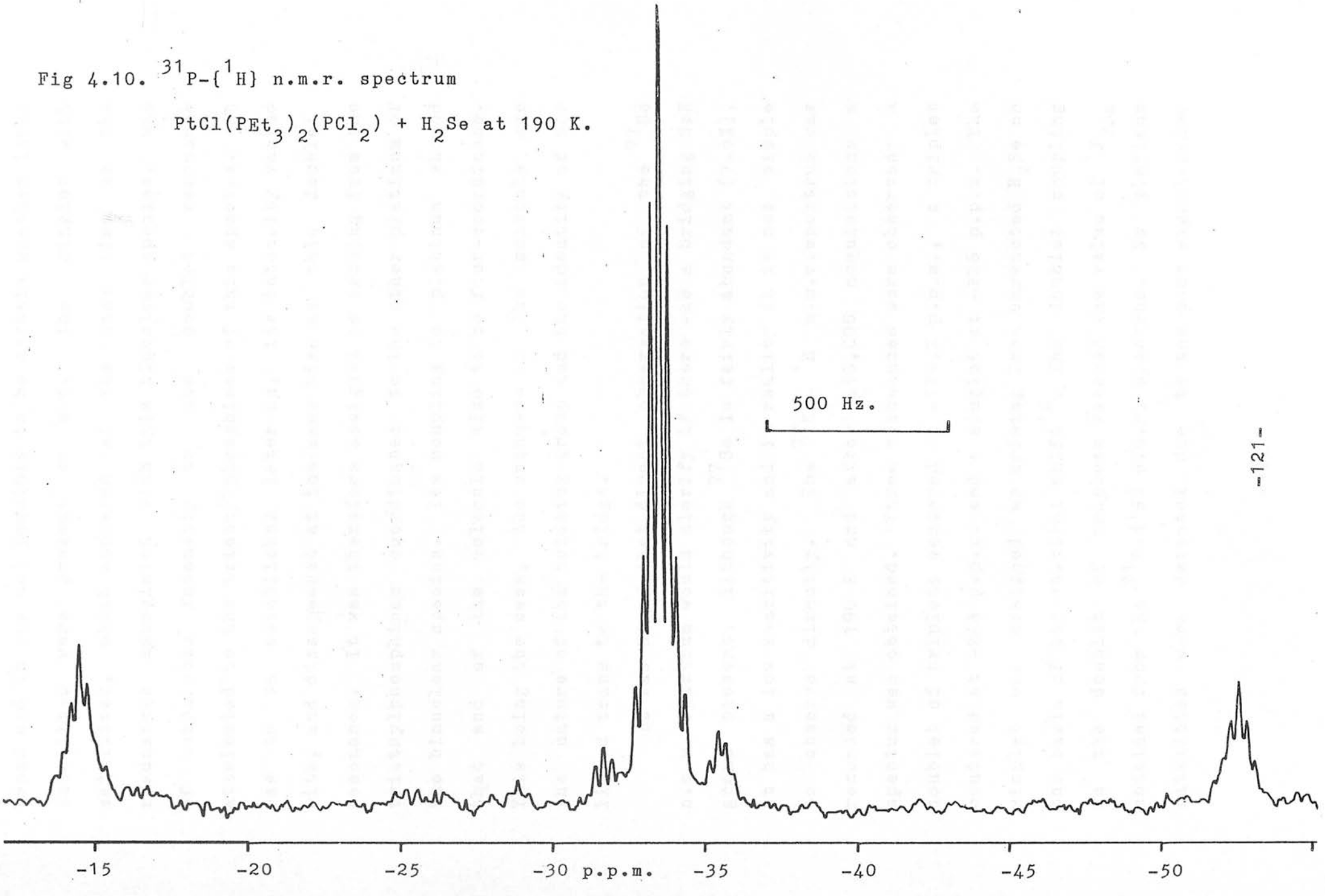
Further warming the solution to 190 K resulted in the dissappearance of the resonances associated with $PtCl(PEt_3)_2(PCl_2)$ and the formation of a new species. A narrow doublet with platinum satellites was centered at +18.8 p.p.m. and the size of the coupling to platinum was indicative of a four-coordinate platinum (II) species. A multiplet with platinum satellites was centered at -33.3 p.p.m. (fig 4.10). A singlet with platinum satellites centered at +16.4 p.p.m. was also detected but not identified. The multiplet resonance was assigned as arising from a triplet with inner platinum satellites whose inner lines overlap with the main triplet giving an unusual intensity pattern. The small patterns to either side of the multiplet were assigned as being ^{77}Se satellites. The presence of the inner set of platinum satellites is indicative of a binuclear platinum species. Retention of proton coupling resulted in a further wide doublet coupling to the multiplet, indicative of four-coordinate phosphorus. The magnitude of the coupling to selenium was indicative of the selenium being directly bound to the unique phosphorus. These facts suggest a structure of the type



The triethylphosphine doublet resonance was rather

Fig 4.10. $^{31}P-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2)$ + H_2Se at 190 K.



broad and it was not possible to be certain whether inner satellites were present or not. The singlet with satellites, which appeared at the same time as the resonances associated with this binuclear species, was of comparable intensity to the doublet resonance attributed to the triethylphosphines of this species. As was to be established later on, its intensity varied with, and dissappeared at the same time as this doublet resonance. It was therefore assigned as arising from the triethylphosphines coordinated to the other platinum of the binuclear species. Its coupling to platinum showed that end of the molecule also to be four-coordinate. This being the case, the unknowns in the molecule are the nature of the bridging group and the identity of the ligand trans to the bridge.

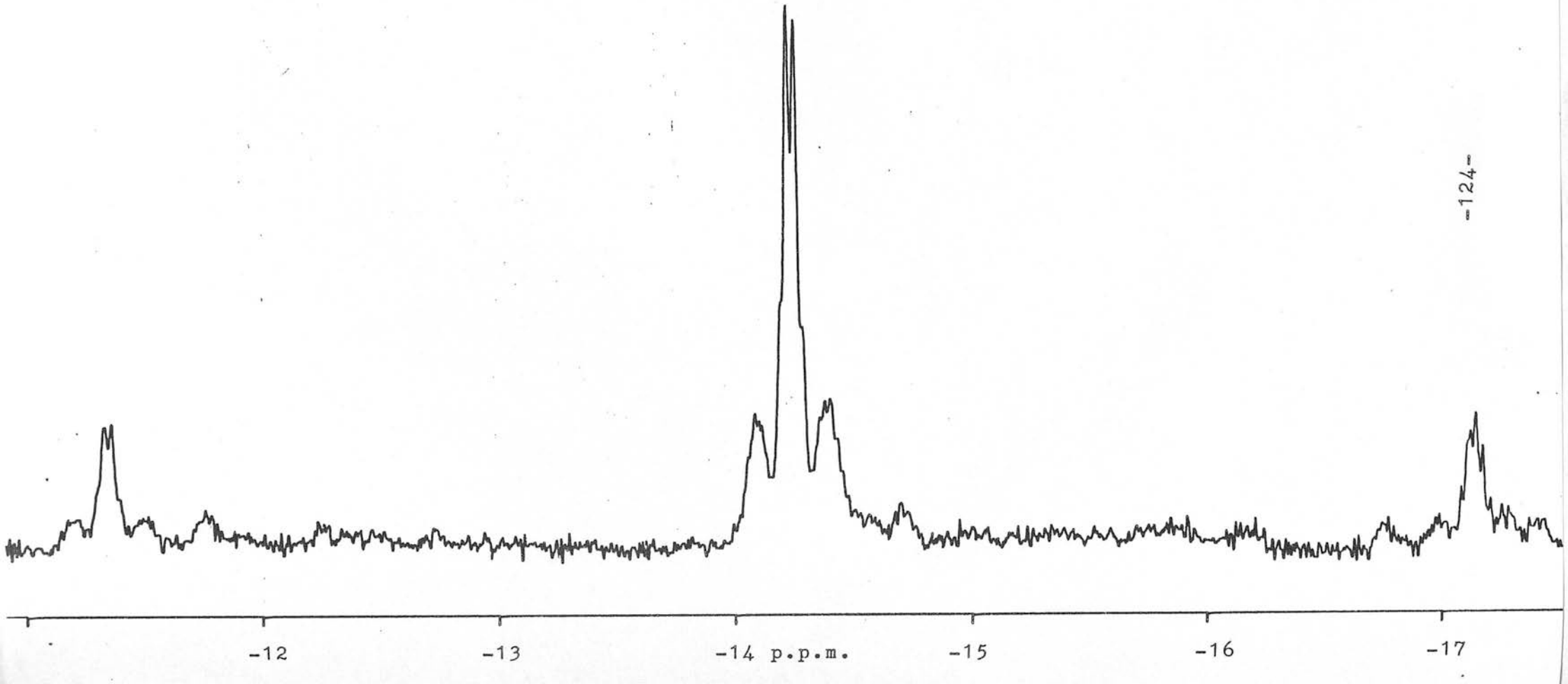
It was hoped thet direct observation of the ^{77}Se n.m.r. spectrum would clarify if there was a bridging SeH group present. Although ^{77}Se is fairly abundant (7.6%), it has a low sensitivity and in reality it is not simple to observe directly. The $^{77}Se-^{1}H$ n.m.r.spectrum was recorded at 190 K and after 450,000 acquisitions a spectum was obtained. Three resonances were observed: A doublet of triplets centered at -178.2 p.p.m., a triplet centered at -248 p.p.m. and a singlet at -226 p.p.m. The singlet was assigned as arising from unreacted H_2Se on the basis of its chemical shift[10]. The doublet coupling in the doublet of triplets matched the value of $^{1}J_{PSe}$ obtained from the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. No platinum satellites were detected due to the poor signal-noise

ratio of the spectrum. The triplet resonance was assumed to arise from the initial cationic product. It was rather surprising to observe the two-bond coupling to the cis triethylphosphines but not that to the trans unique phosphorus. The absence of ^{77}Se satellites on the unique phosphorus resonance in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum had prepared us for failing to see this coupling in the $^{77}Se-\{^{1}H\}$ n.m.r.spectrum. Once again platinum satellites could not be detected. Due to the time taken to obtain the proton decoupled spectrum, it was deemed to be impractical to run the ^{77}Se n.m.r. spectrum with proton coupling retained. The low temperature at which the spectrum had to be recorded precluded running the spectrum overnight.

This information would appear to preclude the possibility of SeH bridging in the binuclear species. Realistically, the bridge would therefore appear to be chloride.

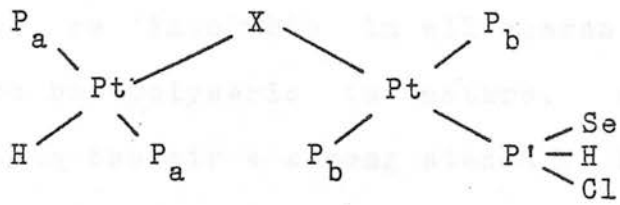
The ^{1}H nmr spectrum of the hydride region showed a rather broad signal at -14.24 p.p.m. with associated platinum satellites. Recording the spectrum at a narrow spectral width and applying line narrowing to the F.I.D. prior to transformation produced a narrow quartet with both inner and outer sets of platinum satellites (fig 4.11). This pattern can be attributed to a hydride trans to the bridge of the binuclear species. The apparent quartet is actually an overlapping doublet of triplets as the value of the four-bond coupling to the trans unique phosphorus is equal to the two-bond coupling to the pair

Fig. 4.11. ^{1}H n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + H_2Se at 190 K.



of cis triethylphosphines.

It thus appears that the structure of the product is -



N.B. P_a & P_b = PEt_3

δP_a = +18.81 p.p.m. δP_b = +16.40 p.p.m.
$\delta P'$ = -33.23 p.p.m. δSe = -178.13 p.p.m.
$\delta P'\underline{H}$ = +7.67 p.p.m. $\delta Pt\underline{H}$ = -14.24 p.p.m.
$^1J_{PtP_a}$ = 2162 Hz. $^1J_{PtP_b}$ = 2560 Hz.
$^1J_{PtP'}$ = 3078 Hz. $^1J_{P'H}$ =386 Hz.
$^1J_{P'Se}$ = 308 Hz. $^2J_{PtH}$ =1164 Hz.
$^2J_{P_aP'}$ =23 Hz. $^2J_{HP_b}$ = 6 Hz.
$^3J_{HPt}$ = 58 Hz. $^3J_{P'Pt}$ = 86 Hz.
$^4J_{HP'}$= 6 Hz.

All parameters were recorded in dichloromethane at 190 K. The n.m.r. parameters of the initial mononuclear product are listed below.

δP = +15.80 p.p.m. $\delta P'$ = +17.27 p.p.m.
δSe = -248.06 p.p.m. $^1J_{PtP}$ = 2994 Hz.
$^1J_{PtP'}$ = 3845 Hz. $^1J_{P'H}$ = 457 Hz.
$^2J_{PP'}$ = 21 Hz.

The initial mononuclear product decomposed as soon as the temperature was raised further but the binuclear product remained stable to a temperature of 250 K. Above

this temperature a yellow solid precipitated out of solution, rendering further spectra impossible to obtain as the instrument would not hold a lock. This yellow material was separated by filtration under nitrogen but proved to be insoluble in all common solvents and was assumed to be polymeric in nature. On bringing the sample into the air a strong stench of hydrogen selenide was noted.

One of the main reasons for carrying out this reaction was to try to prepare a comparable species to that obtained in the reaction with hydrogen sulphide. It appeared that in this respect the attempt had been unsuccesful unless the species had not been observed due to the large number of resonances present. Accordingly it was decided to repeat the reaction and observe the $^{31}P-\{^{1}H\}$ n.m.r. spectrum using a DEPT (Distortionless Enhancement by Polarisation Transfer) pulse sequence.[11] DEPT sequences are normally used in ^{13}C n.m.r. spectroscopy but the presence of a one-bond phosphorus-hydrogen coupling in all of the molecules of interest means the technique can be applied in this instance. The consequence of using the DEPT sequence is that all molecules containing a one-bond phosphorus hydrogen coupling will have their intensity enhanced at the expense of all other signals. Ideally no other signals should show but this relies on all of the phosphorus hydrogen couplings being the same. As the two species already detected have different couplings to hydrogen, an average value was inserted into the pulse

sequence as $^{1}/2J$. The resultant spectrum (fig.4.12) showed the desired enhancement of the signals attributable to unique phosphorus atoms but no new signals were detected. Although this experiment was unsuccesful, the technique should prove applicable to many other systems.

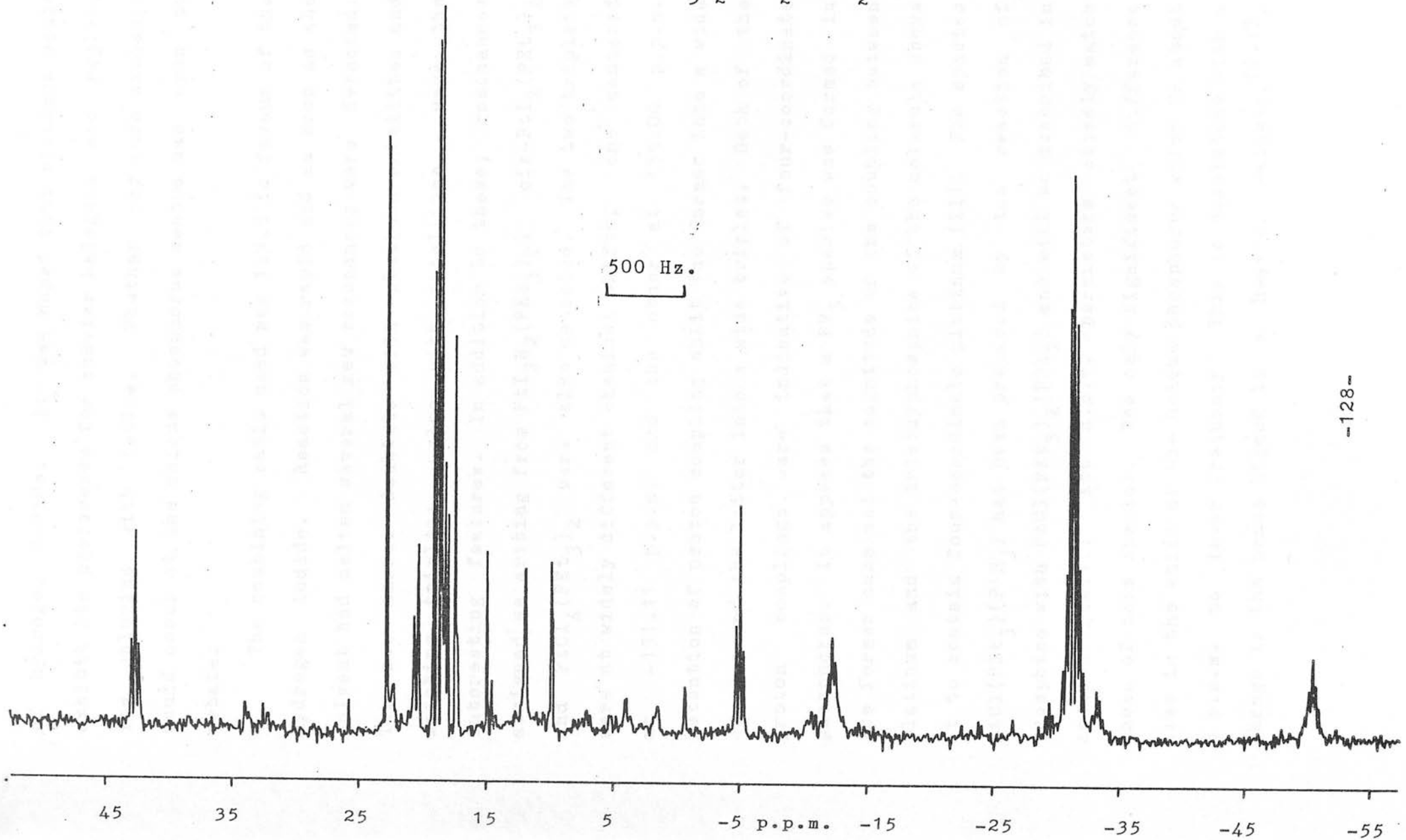
The two compounds mentioned both have unique phosphorus atoms which are chiral. As in the case previously described in section 4.2.5, no effect of this chirality could be detected on the $^{31}P-\{^{1}H\}$ n.m.r. spectrum and although the selenium and chlorine are quite different, for some other reason the second order effect does not manifest itself.

The mechanism of formation of the binuclear product is not clear but may involve $PtCl_2H_2(PEt_3)_2$ as it is the only species present containing a hydride. However, the presence of H_2Se always presents other possible routes for generating a hydrido-species and at this time no firm suggestions can be offered.

4.2.8. Reaction with Hydrogen iodide

As described previously, reaction with excess hydrogen chloride results in the protonation of the unique phosphorus. The results presented in chapter 3 of this work describe the characterisation the analogous species $PtBr(PEt_3)_2(PBr_2H)^{+}$. No mention was made of the corresponding iodo species; the virtual insolubility of phosphorus triiode prevented the reaction between it and $PtHI(PEt_3)_2$. In an attempt to prepare some iodo species, it was decided to react $PtCl(PEt_3)_2(PCl_2)$ with an excess

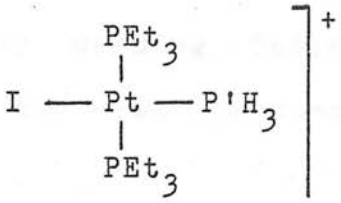
Fig. 4.12. ^{31}P DEPT n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2) + H_2Se$



of hydrogen iodide. It was hoped that platinum would exhibit its preference for heavier halogens and replace its chlorine with iodine. Whether any such exchange would occur at the unique phosphorus centre was open to debate.

The combining ratio used was 1:3.5 in favour of the hydrogen iodide. Reaction was rapid and as soon as the solvent had melted several new resonances were detected. Two new narrow doublets with platinum satellites and matching triplets, also with satellites, were the interesting features. In addition to these, resonances assigned as arising from $PtI_2H_2(PEt_3)_2$, cis-$PtI_2(PEt_3)_2$ and $PtCl_4(PEt_3)_2$ were also detected. The two triplets were at widely different chemical shifts, one centered at -131.11 p.p.m. and the other at +55.00 p.p.m. Retention of proton coupling split the former into a wide quartet and the latter into a wide triplet. Both of the proton couplings were indicative of four-coordinate phosphorus. It appears that a PH_3 species was formed in the former case and the magnitude of the coupling between platinum and the triethyphosphine of the molecule shows it to contain four-coordinate platinum (II). The species $PtCl(PEt_3)(P'H_3)$ has been prepared by the reaction of phosphine with $PtCl(PEt_3)_2(PCl_2)$ and will be described in section 4.2.11; its n.m.r. parameters closely match those of this species. The only significant difference lies in the shift of the unique phosphorus which is about 6 p.p.m. to lower frequency. This is consistent with a change in the trans ligand to a heavier halogen.[12,13].

The species was assigned as



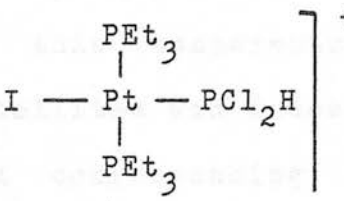
$\delta P = +17.01$ p.p.m. $\quad \delta P' = -131.11$ p.p.m.

$^1J_{PtP} = 1980$ Hz. $\quad ^1J_{PtP'} = 3344$ Hz.

$^1J_{P'H} = 436$ Hz. $\quad ^2J_{PP'} = 28$ Hz.

All parameters were recorded in dichloromethane at 180 K. No proton parameters are included as these were very similar to those of the chloro analogue.

The n.m.r. parameters of the other new species were very similar to those for $PtCl(PEt_3)_2(PCl_2H)^+$. The difference in the shifts of the unique phosphorus resonances was 10.5 p.p.m. Although the shift of the unique phosphorus of the chloro cation is known to vary with HCl concentration and temperature, it was thought that this was a slightly different species due to variation in the other n.m.r. parameters. The structure was assigned as being :-



$\delta P = +23.49$ p.p.m. $\quad \delta P' = +55.00$ p.p.m.

$^1J_{PtP} = 1998$ Hz. $\quad ^1J_{PtP'} = 4711$ Hz.

$^1J_{P'H} = 531$ Hz. $\quad ^2J_{PP'} = 24$ Hz.

All parameters were recorded in dichloromethane at 180 K. Once again the proton parameters were so similaar to the chloro analogue that they are not listed. This similarity strongly suggests that it is only the halogen

on the platinum which has been exchanged.

Further warming failed to produce any other new species and the two products gradually decomposed by 270 K.

4.2.9. Reaction with Ammonia.

In the reaction between $PtCl(PEt_3)_2(PCl_2)$ and HCl, the $-PCl_2$ group acted as a basic centre and was protonated. This behavior can be attributed to the lone pair on the unique phosphorus. Accordingly, any reaction with ammonia was thought unlikely to involve the lone pair but more likely to involve substitution of one of the chlorine atoms in an manner analogous to the reaction of phosphorustrichloride with dimethylamine

$$PCl_3 + 2HN(CH_3)_2 \longrightarrow Cl_2PN(CH_3)_2 + H_2N(CH_3)_2^+Cl^-$$

This would then give rise to the possibility of replacing the $-NH_2$ group with other groups such as -F.

Reaction was slow and no change was detected in the $^{31}P-\{^1H\}$ n.m.r. spectrum until the temperature reached 230 K. At this temperature, a narrow doublet with platinum satellites was detected at 16.42 p.p.m. but no trace of a corresponding triplet resonance could be found. It was concluded that the product contained four-coordinate platinum(II) on the basis of the size of the platinum-phosphorus coupling constant. Further warming resulted in an increase in the concentration of the doublet resonance but still no trace of any other resonance. Retention of proton coupling broadened the triethylphosphine resonance but still failed to reveal

the presence of any other resonance.

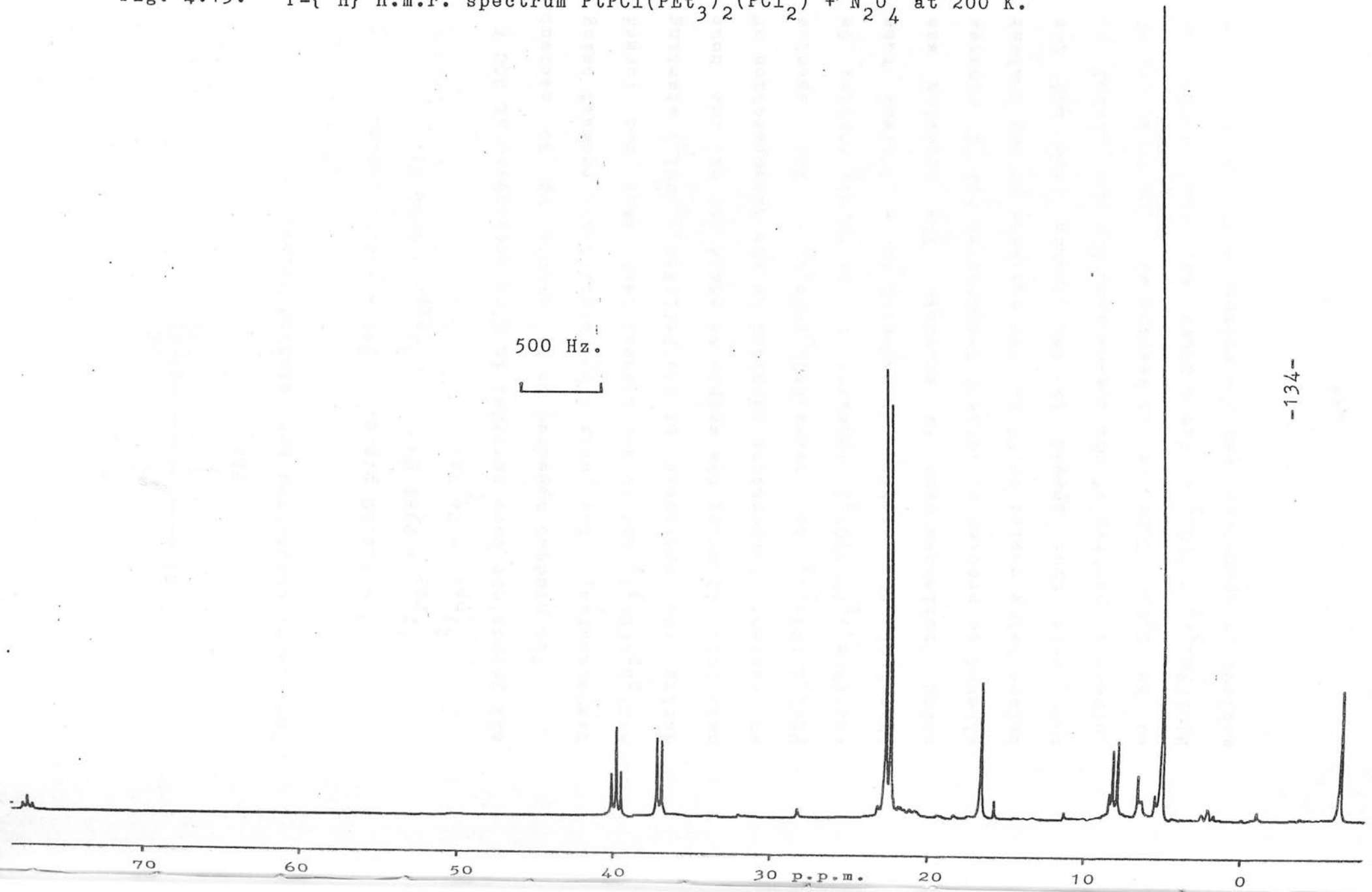
One possible explanation for the failure to detect the associated unique phosphorus resonance is that if the desired reaction had occurred, then the unique phosphorus would be directly bonded to a nitrogen atom. ^{14}N is a quadropolar nucleus with I = 1 and as such would tend to broaden the resonance of the unique phosphorus to which it was bound. In the extreme case, the broadening might be so great that the resonance could not be detected. Accordingly the reaction was repeated using 95% $^{15}NH_3$. ^{15}N has spin $^1/2$ and so will not broaden the phosphorus signal. Observing the $^{31}P-\{^1H\}$ n.m.r. spectrum showed virtually identical behavior to the reaction with normal ammonia. Even at ambient temperature, prior to decomposition, no trace could be found of a unique phosphorus resonance. This leaves the only explanation to be some sort of exchange mechanism in which the chemical shift difference between the two unique phosphorus signals is so great that the resonance is too broad to be detected. However, this must also mean that the differences in both shift and platinum couplings of the triethylphosphine signals between the two species are very small. No detectable broadening in either the central resonance or either of the platinum satellites could be detected. This is in contrast to the effect obseved in section 4.2.4. In an attempt to slow down this proposed exchange process, the sample was cooled down to 173 K but with no success. In an attempt to reduce the temperature still further, the reaction

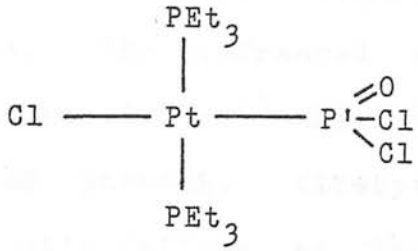
was repeated in a mixture of dichloromethane and diethylether whose freezing point was known to be 153 K. Regretably, the reaction did not proceed by the same route in the mixed solvent and the desired species failed to form. The reaction resulted in the gradual decomposition of the $PtCl(PEt_3)_2(PCl_2)$. In view of the failure to rationalise this reaction it was decided not to carry out any further work on this system.

4.2.10. Reaction with Dinitrogen tetroxide.

Reaction was rapid and by 200 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed all of the $PtCl(PEt_3)_2(PCl_2)$ to have been consumed. In addition to resonances associated with $PtCl_2H_2(PEt_3)_2$, a new narrow doublet and triplet, both with platinum satellites, were observed. (fig.4.13) The platinum coupling to the unique phosphorus was unusually large at 6024 Hz whilst that to the triethylphosphine resonance was typical for a four coordinate platinum(II) species. Retention of proton coupling broadened the triethylphosphine signal but had no effect on the unique phosphorus resonance. The analogous reaction between $Ir(CO)Cl_2(PEt_3)_2(PCl_2)$ and dinitrogen tetroxide[4] produced a species which was isolated and identified by X-ray crystallography as being $Ir(CO)Cl_2(PEt_3)_2(P(O)Cl_2)$. Comparison of the relevant parameters for this species with those obtained in the platinum case make it seem likely that an analogous reaction has occured producing the species

Fig. 4.13. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtPCl(PEt_3)_2(PCl_2)$ + N_2O_4 at 200 K.





The n.m.r. parameters are detailed below.

$\delta P = +22.40$ p.p.m. $\quad \delta P' = +39.50$ p.p.m.

$^1J_{PtP} = 2388$ Hz. $\quad ^1J_{PtP'} = 6024$ Hz.

$^2J_{PP'} = 24$ Hz.

All parameters were recorded in dichloromethane at 200 K

The product appeared to be stable up to ambient temperatures, the only other significant product being $PtCl_2H_2(PEt_3)_2$ and it was assumed that this had formed during the synthesis of the $PtCl(PEt_3)_2(PCl_2)$ starting material. Allowing the sample to stand for ca. one hour at ambient temperature resulted in the decomposition of $PtCl_2H_2(PEt_3)_2$ to trans-$PtCl_2(PEt_3)_2$. The species $PtCl(PEt_3)_2(P(O)Cl_2)$ appeared to be fairly stable. On this basis the reaction was repeated in a Schlenk tube using dichloromethane as solvent. The reaction was allowed to proceed at ambient temperature for 10 minutes before being cooled to 77 K. The contents of the Schlenk tube were then opened to the vacuum line and the infra-red spectrum of the non-condensible gas showed it to be N_2O. This is in keeping with the formation of $PtCl(PEt_3)_2(P(O)Cl_2)$. The mixture was then warmed to ambient temperature and the solvent distilled off under

reduced pressure. The resulting oil was then triturated in a mixture of hexane and diethylether to yield a bright yellow solid. The infra-red spectrum of the product showed a band at 1220 cm^{-1} which was assigned as arising from the P=O stretch. Attempts to obtain a FAB mass spectrum met with failure as the product appeared to react with the glycerol support medium. This is a known problem with FAB mass spectra[12,13] and adding glycerol to a sample of $PtCl(PEt_3)_2(P(O)Cl_2)$ and running the $^{31}P-\{^1H\}$ n.m.r. spectrum showed that the product decomposed at ambient temperature. Attempts to obtain a mass spectrum by conventional ionisation also met with failure as the sample decomposed on heating. It did not prove possible to separate the product from the $PtCl_2H_2(PEt_3)_2$ impurity and so elemental analysis was not possible. Despite these problems, the n.m.r. and i.r. evidence combined with the iridium analogy leave little room for doubt as to the identity of the product.

4.2.11. Reaction with Phosphorus Pentachloride

Due to the failure to add chlorine oxidatively to the unique phosphorus of $PtCl(PEt_3)_2(PCl_2)$, it was decided to try the reaction with phosphorus pentachloride. Phosphorus pentachloride is known to act as a chloride ion donor in the presence of a chloride ion acceptor and in the solid phase exists as $(PCl_4)^+(PCl_6)^-$[16]. Pilkington[4] found that reaction of phosphorus pentachloride with $Ir(CO)Cl_2(PEt_3)_2(PCl_2)$ gave

$[Ir(CO)Cl_2(PEt_3)_2(PCl_3)]^+$ as the major product.

Reaction was rapid and at 190 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed a mixture of $PtCl(PEt_3)_2(PCl_2)$, PCl_3, $(PCl_6)^-$ and $PtCl_4(PEt_3)_2$. No resonance was detected for PCl_5. Further warming resulted in the production of a mixture of PCl_3 and $PtCl_4(PEt_3)_2$. No further reaction occurred and the reaction was not deemed worth further investigation.

4.2.12. Reaction with Phosphorus Pentafluoride.

Reaction was rapid and at 180 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed, in addition to resonances attributable to $PtCl(PEt_3)_2(PCl_2)$, small amounts of PCl_3 and $PtCl(PEt_3)_2(PCl_2H)^+$. Further warming the sample to 200 K resulted in the formation of OPF_3 and a very broad hump centered around -150 p.p.m. Superimposed on this hump were a series of apparently unrelated peaks. None of these peaks appeared to have platinum satellites but some appeared to be separated by amounts which may have corresponded to phosphorus(V)-fluorine couplings. Retention of proton coupling had no effect whatsoever on this region. Further increasing the temperature to 220 K resulted in the starting material resonances broadening as the familiar exchange process occured. Further warming resulted in the immediate decomposition of the platinum species leaving a mixture of OPF_3, PF_3 and cis and trans $PtCl_2(PEt_3)_2$.

The absence of detectable amounts of HCl in the

phosphorus pentafluoride starting material may mean that the protonated cation was formed by reaction with HF rather than HCl. Although the low temperature $^{19}F-\{^{1}H\}$ n.m.r. spectrum did not show a resonance which could definitely be assigned to F^-, there were two unassiged singlets which may have arisen from this source. The doubt arises from the variable positon of the F^- ion resonance with a variety of factors. Allowing for the formation of HF in the reaction mixture may also account for the strange low frequency resonances in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. This may result in the formation of complex ionic phosphorus(V) fluoro species. The reaction of HF with the glass n.m.r. tube would liberate SiF_4 which accounts for one of the unidentified peaks in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum . The liberated water then accounts for the formation of OPF_3 and a combination of this and HF may explain the rapid demise of the platinum species as the mixture warmed.

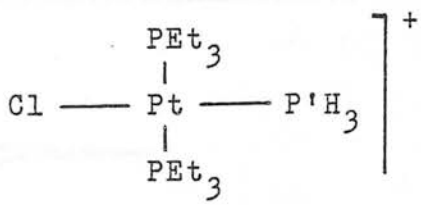
4.2.13. Reaction with Phosphine

This reaction was studied with various molar ratios of phosphine and each reaction will be dealt with separately.

(i) Reaction with 1 equivalent of phosphine.

Reaction was rapid and at 180 K the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed starting material and a small amount of PCl_3. In addition to this, a new narrow doublet with platinum satellites was centered at +17.48 p.p.m. The

magnitude of the coupling to platinum confirmed that the species contained four-coordinate platinum(II). A corresponding narrow triplet , also with platinum satellites, was centered at -124.18 p.p.m. This chemical shift was quite different from the others observed in this series of reactions. Retention of proton coupling split this resonance into a further wide quartet (fig. 4.14). The magnitude of the proton coupling was indicative of four-coordinate phosphorus, indicating the presence of coordinated phosphine. The ^{1}H nmr spectrum at this temperature showed a doublet of triplets with platinum satellites (fig.4.15) centered at +4.59 p.p.m. and no trace of a low frequency hydride could be detected. No further couplings were detected in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum and it therefore seemed likely that the remaining ligand was a chloride giving the structure as the mono cation :-



$\delta P = +17.48$ p.p.m. $\quad \delta P' = -124.18$ p.p.m.

$\delta H = +4.59$ p.p.m. $\quad {}^{1}J_{PtP} = 1994$ Hz.

${}^{1}J_{PtP'} = 3362$ Hz. $\quad {}^{1}J_{P'H} = 430$ Hz.

${}^{2}J_{PP'} = 28$ Hz. $\quad {}^{2}J_{PtH} = 26$ Hz.

${}^{3}J_{PH} = 6$ Hz.

All parameters were recorded in dichloromethane at 180 K

The formation of this species appears to be analogous to the reactions of $PtHX(PEt_3)_2$ (X = halogen)

Fig.4.14. ^{31}P n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + PH_3 at 180 K.

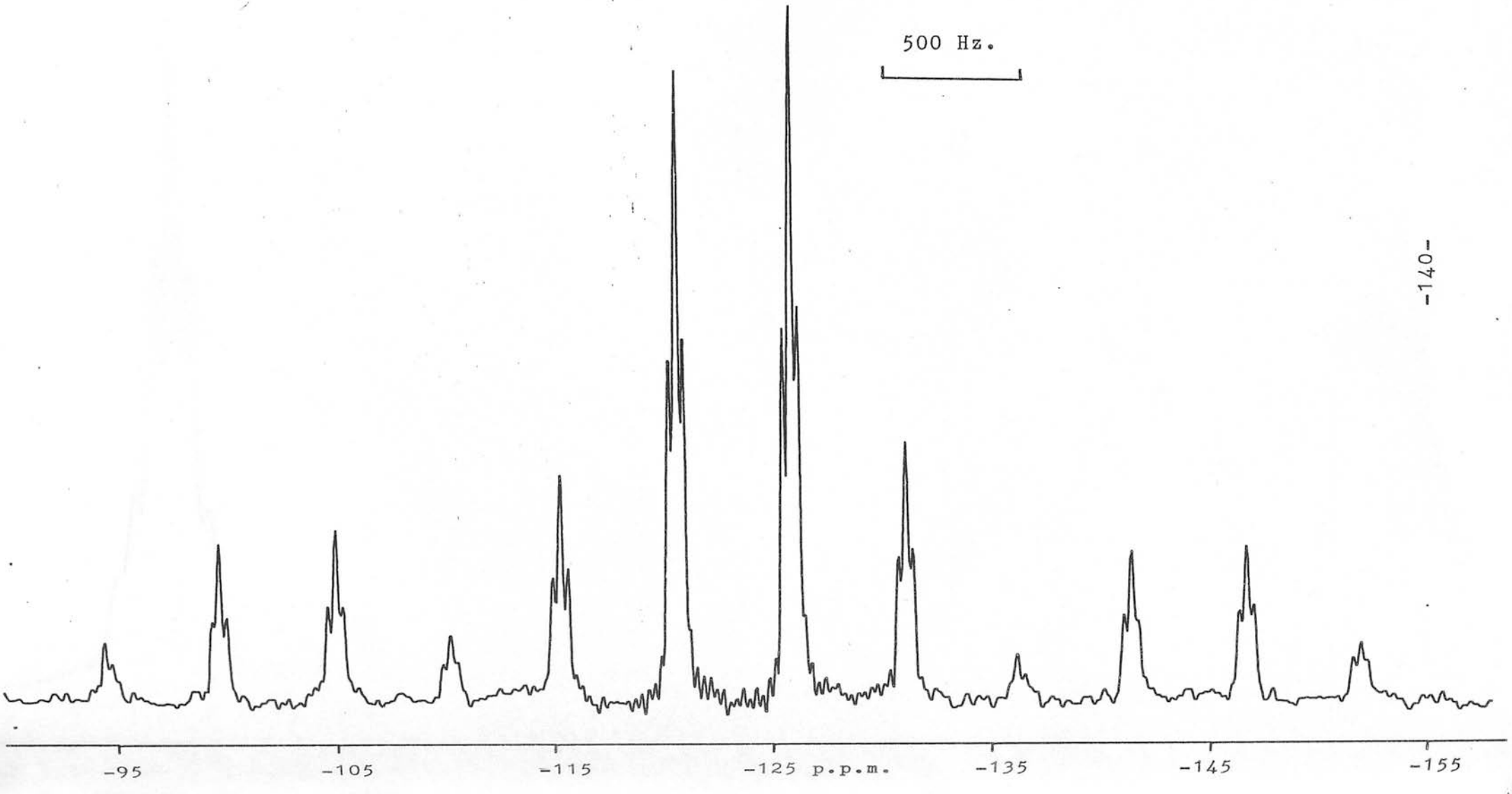
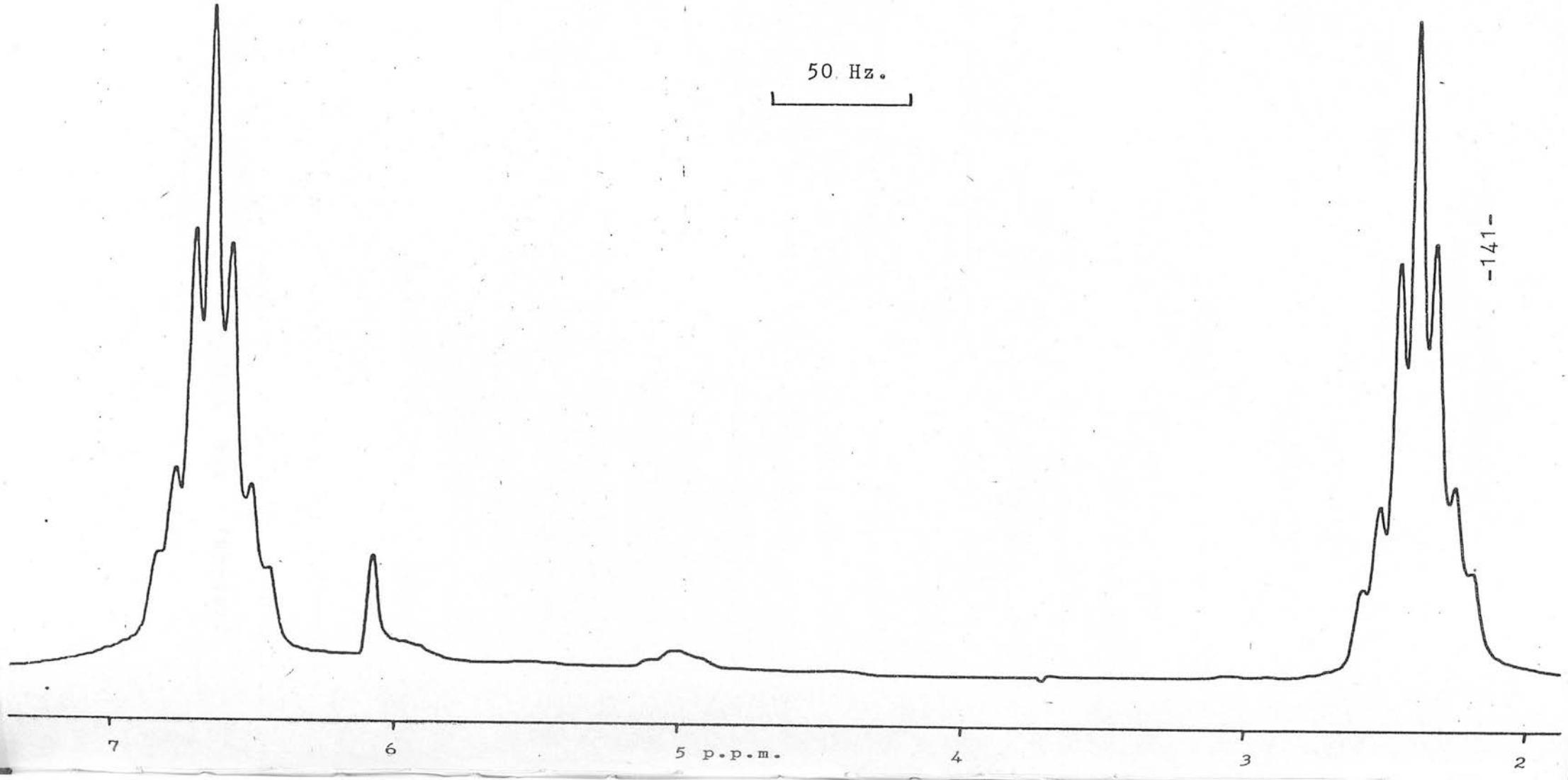


Fig. 4.15. ^{1}H n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + PH_3 at 180 K.



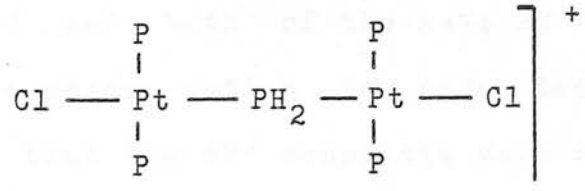
with phosphine[17] in which the halide was displaced yielding a series of mono cations. In these reactions, the counter anion was the displaced halide. In the above rection, the displaced ligand is $-PCl_2$. The $^{31}P-\{^1H\}$ n.m.r. spectrum failed to show a resonance which could be assigned to this species. It seemed likely that the PCl_2 group had disproportionated to PCl_3, Cl^- and $(PCl)_n$ polymer. Indeed, when the tube was removed from the probe a familiar insoluble yellow material was seen to have formed. Further warming of the sample to 200 K resulted in the formation of small amounts of $PtCl(PEt_3)_2(PCl_2H)^+$. Further warming resulted in the familiar broadening of the unique phosphorus resonances as an exchange process became established. The H^+ presumably came from the PH_3 by some sort of disproportionation reaction. The reaction mixture remained stable up to a temperature of 270 K. Above this temperature the species decomposed to yield the normal products.

In order to test the assignment of the structure as the phosphine cation above, the reaction between PH_3 and trans $PtCl_2(PEt_3)_2$ was studied by $^{31}P-\{^1H\}$ n.m.r. spectroscopy at 200 K. The sole product so obtained had n.m.r. parameters identical to those of the aforementioned product and the assignment was assumed to be correct.

(ii) Reaction with 2 equivalents of phosphine.

Once again reaction was rapid and at 180 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed the presence of

$PtCl(PEt_3)_2(PCl_2)$, PCl_3, $PtCl_2H_2(PEt_3)_2$ and the PH_3 species described above. Warming the solution resulted in the broadening of the high frequency resonance of $PtCl(PEt_3)_2(PCl_2)$ associated with exchange. No further change was detected in the $^{31}P-\{^1H\}$ n.m.r. spectrum until the temperature reached 230 K. Two new narrow doublets, both with platinum satellites, were observed in the triethyl phosphine region. Two new unique phosphorus resonances, also with platinum satellites, were also detected. Retention of proton coupling further split both of these resonances into wide triplets of different coupling. The lower frequency signal and its associated triethyl phosphine resonance were assigned as arising from $ClPt(PEt_3)_2(PH_2Cl_2)$ on the basis of parameters obtained in Chapter 3. This had presumably formed from the interaction of $PtCl(PEt_3)_2(PCl_2)$ with $PtCl_2H_2(PEt_3)_2$ as previously described. The other unique phosphorus resonance appeared to have an anomalous intensity pattern and observing the resonance under higher resolution conditions revealed the actual pattern to be a quintet with platinum satellites. Comparison of the parameters with those obtained for the product of the reaction between BCl_3 and $PtCl(PEt_3)_2(PCl_2)$ showed the species to be



$(P = PEt_3)$

The counter anion was assumed to be chloride but

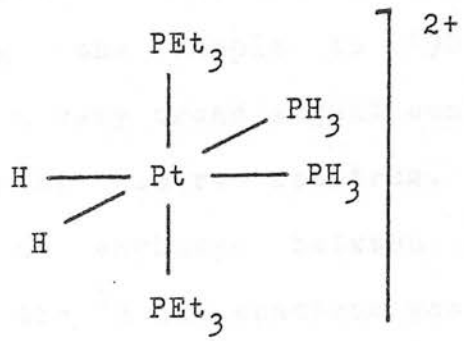
this was not verified. The mechanism whereby this species is formed in this reaction does not seem to be in keeping with the presence of excess phosphine. A mechanism involving reaction of the initial phosphine cation with a platinum species can be postulated but would be deemed more likely in the presence of lower concentrations of phosphine. The concentration of the cationic phosphine product relative to unreacted $PtCl(PEt_3)_2(PCl_2)$ appeared to be approximately the same in both reactions. No rational can be offered to account for this behaviour.

Increasing the temperature resulted in an increase in the concentration of the binuclear cation at the expense of the other species present until at 260 K it was major component of the mixture. Above this temperature, decomposition was rapid and resulted in the usual mixture of products.

(iii) Reaction with 4 equivalents of phosphine.

Reaction was again rapid and at 180 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed $PtCl(PEt_3)_2(PCl_2)$, $PtCl(PEt_3)_2(PH_3)^+$ and free phosphine. This was the first of these reactions in which phosphine had been detected. Re-running the spectrum a few minutes later, still at 180 K, showed all the $PtCl(PEt_3)_2(PCl_2)$ to have been consumed and both of the sets of resonances associated with the chloro cation to have broadened to such an extent that the PP' couplings were no longer visible. A narrow triplet with platinum satellites was centered at +1.0 p.p.m. and another triplet, with the same coupling,

with platinum satellites was centered at -161.1 p.p.m. The magnitude of the platinum coupling to the triethylphoshine resonance was indicative of a six-coordinate platinum (IV) species. This resonance broadened on retention of proton coupling but the low frequency triplet further split into an apparent doublet of quartet of multiplets. Closer examination of this pattern under high resolution conditions revealed a complex second order pattern. The ^{1}H nmr spectrum of the hydride region revealed a broad doublet with platinum satellites. Line narrowing the spectrum showed complex structure to be present but it was not possible to fully resolve it at this temperature. The $P\underline{H}_3$ region of the ^{1}H nmr spectrum showed a complex doublet resonance which again could not be analysed partly due to the breadth associated with the temperature and partly due to the presence of overlapping lines. Once again, line narrowing techniques were unsuccesful. The doublet coupling matched that obtained from the proton coupled $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the low frequency region. Collectively, these facts suggest the product was



The two PH_3 groups are magnetically equivalent as long as

the protons are decoupled. If the proton coupling is retained, however, they become magnetically inequivalent althogh still chemically equivalent. This results in a very complex second order ^{31}P n.m.r. spectrum of the type described. The ^{1}H nmr spectrum of the hydrides is similarly complex. These patterns in general do not allow for direct measurement of coupling constants, they have to be obtained by synthesising the theoretical spectrum and varying the parameters until the result matches the experimental spectrum. This was not possible, as a high enough quality experimental spectrum could not be obtained. An apparent sharp intense doublet centered at -211.6 p.p.m. had also developed. This resonance did not appear to have platinum satellites. Retention of proton coupling resulted in this signal splitting into an apparent quartet which was presumably two overlapping triplets. No corresponding couplings could be detected in the ^{1}H nmr spectrum and they were assumed to be overlapped by the broad triethyl phosphine resoanaces. No clue can be offered as to the identity of this species but as it does not contain platinum it was decided to ignore it for the time being.

Warming the sample to 190 K resulted in the formation of a very broad signal centered at -230 p.p.m. in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. This was assigned as arising from an exchange between PH_3 and PH_4^+. The quality of the ^{1}H nmr spectrum was still poor. Warming to 200 K resulted in the disapearance of the resonances associated with the six-coordinate species, leaving the

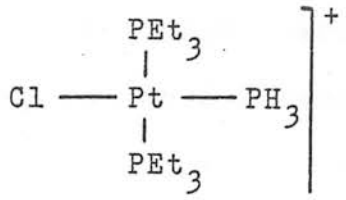
chlorophosphine cation as the only species containing a unique phosphorus atom. A singlet assigned as $HPEt_3^+$, and a resonance due to free triethylphosphine were observed in addition to the broad hump at -230 p.p.m. Further warming resulted in the contents of the tube turning bright orange and solidifying making it impossible to collect any further spectra.

At this point it was decided not to carry out any further reactions with other stoichiometries of phosphine. The reaction pathway is obviously very dependant on the concentration of phosphine and would certainly bear further investigation at some later date.

4.2.14. Reaction with Trimethyl stannane.

Trialkylstannanes and trialkylgermanes have been used to reduce platinum halide bonds to platinum-hydride bonds.[18,19] As such this was seen as a potential route to another series of novel compounds via the formation of $PtH(PEt_3)_2(PCl_2)$. The possibility of reduction of one or both of the phosphorus-chlorine bonds was recognised but such a reaction would also produce a novel species.

Reaction was rapid, and as soon as the solvent had melted the $^{31}P-\{^1H\}$ n.m.r. spectrum showed, in addition to $PtCl(PEt_3)_2(PCl_2)$, a further narrow doublet and triplet, both with platinum satellites. From previous reactions in this chapter, the product was identified as



Further warming resulted in the broadening of the unique phosphorus resonance of $PtCl(PEt_3)_2(PCl_2)$ as it exchanged with HCl. Retention of proton coupling showed the protonated form. Further warming merely resulted in the normal pattern of the exchange reaction already described. At 260 K, resonances were detected which were assigned as arising from the PH_2-bridged binuclear species produced in the reaction between $PtCl(PEt_3)_2(PCl_2)$ and diborane. Warming further resulted in decomposition of the products by the normal route.

It appears that the $-PCl_2$ group was fully reduced by the trimethylstannane and the platinum chlorine bond was unaffected. Repeating the reaction with a two-fold excess of trimethylstannane in an attempt to reduce this bond was unsuccesful. Studying the initial reaction at lower temperatures failed to reveal a partially reduced $-PCl_2$ group and no further work was carried out on this system.

4.2.15. Reaction with Trityl tetrafluorobrate.

Recent work in this department [20] used the title compound to remove a chloride ion from a coordinated $PClN(CH_3)_2$ to produce a novel ionic species with an unusual $^{31}P-\{^1H\}$ n.m.r. shift of +695 p.p.m. Reaction between $PtCl(PEt_3)_2(PCl_2)$ and trityl tetrafluoroborate was studied from 180 K to ambient temperatures. No

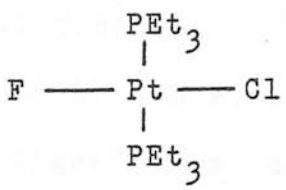
reaction was detected before the $PtCl(PEt_3)_2(PCl_2)$ decomposed by the normal route.

4.2.16. Reaction with Xenon difluoride.

The use of xenon difluoride as a mild fluorinating agent has been reported previously.[21,22] Recent work in this department has produced the species $Ir(CO)Cl_2(PEt_3)_2(PF_4)$ by the reaction of xenon difluoride with $Ir(CO)Cl_2(PEt_3)_2(PCl_2)$. This appears to have occured by simple oxidative addition of F_2 across the unique phosphorus atom. It was therefore hoped to carry out the analogous addition to $PtCl(PEt_3)_2(PCl_2)$. The desired reaction would be to produce $PtCl(PEt_3)(PF_2)$ and hopefully to add F_2 across its unique phosphorus. Regretably, terminal $-PF_2$ platinum species have so far eluded synthesis.

The exact stoichiometry of this reaction was difficult to determine, due to the difficulties encountered in transferring the xenon difluoride which had to be added as a solid to the solution of $PtCl(PEt_3)_2(PCl_2)$ held at 77 K. The error was probably within 10%. Reaction was slow until 210 K when the $^{31}P-\{^1H\}$ n.m.r. spectrum showed the presence of $PtCl(PEt_3)_2(PCl_2)$, $PtCl_2H_2(PEt_3)_2$ and a new doublet with platinum satellites centered at +25.10 p.p.m. No further new resonances could be detected. Retention of proton coupling broadened this signal but still failed to show any other new signals. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II)

species. Initially this suggested that the other resonance was lost due to exchange-induced broadness. Observing the $^{19}F-\{^{1}H\}$ n.m.r. spectrum showed a narrow triplet with platinum satellites centered at -339.1 p.p.m. Previous work[23] has shown that fluorine bonded directly to a transition metal resonates in this part of the $^{19}F\{^{1}H\}$ n.m.r. spectrum. Retention of proton coupling had no significant effect on the resonance and the triplet coupling matched the doublet coupling observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. Recent work in this department[24] studied the reaction between xenon difluoride and trans $PtCl_2(PEt_3)_2$. One of the products from this reaction had n.m.r. parameters identical to those of the above species. Based on these facts, the structure was assigned as



$\delta P = +25.10$ p.p.m. $\quad \delta F = -339.10$ p.p.m.

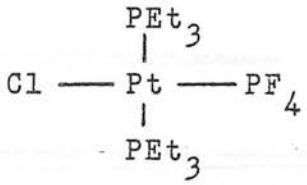
$^{1}J_{PtP} = 2814$ Hz. $\quad ^{1}J_{PtF} = 1161$ Hz.

$^{2}J_{PF} = 20$ Hz.

Parameters were recorded in dichloromethae at 210 K

Further warming the sample to 230 K and observing the $^{31}P-\{^{1}H\}$ n.m.r. spectrum showed resonances attributable to PF_3, PF_6^- and $PtCl(PEt_3)_2(PCl_2O)$. In addition to these resonances there was also a new doublet with platinum satellites centered at +22.60 p.p.m. The species was assigned as containing four-coordinate platinum on the basis of the coupling to platinum.

Additionally there was a quintet of triplets with platinum satellites, not all of which could be resolved fromthe main resonances, centered at +13.00 p.p.m. Retention of proton coupling had no effect on this resonance other than to clarify the positions of some of the satellite lines (fig.4.16). This implies the presence of the species :-



In the iridium-PF_4 species previously discussed, the PF_4 phosphorus resonated at -72 p.p.m., which is substantially different from the shift observed in the platinum species. This may be a consequence of the difference in the coordination numbers at the metals and a variety of other factors.

Observing the $^{19}F-\{^1H\}$ n.m.r. spectrum showed resonances which were assigned as arising from PF_3, PF_6^-, $PtClF(PEt_3)_2$ and a trace of OPF_3 on the basis of their n.m.r. parameters. In addition to these resonances there was a very broad hump centered about -10 p.p.m. (fig.4.17). This hump was approximately 2000 Hz. wide at half height. This suggested that the fluorines coordinated to the unique phosphorus were fluxional. Assuming square planar geometry at the platinum centre and trigonal bipyramidal geometry at the unique phosphorus with the metal in an equitorial position, there should be two distinct types of fluorine atoms. i.e. axial and equitorial (fig.4.18.).

Fig.4.16. ^{31}P n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + XeF_2 at 240 K.

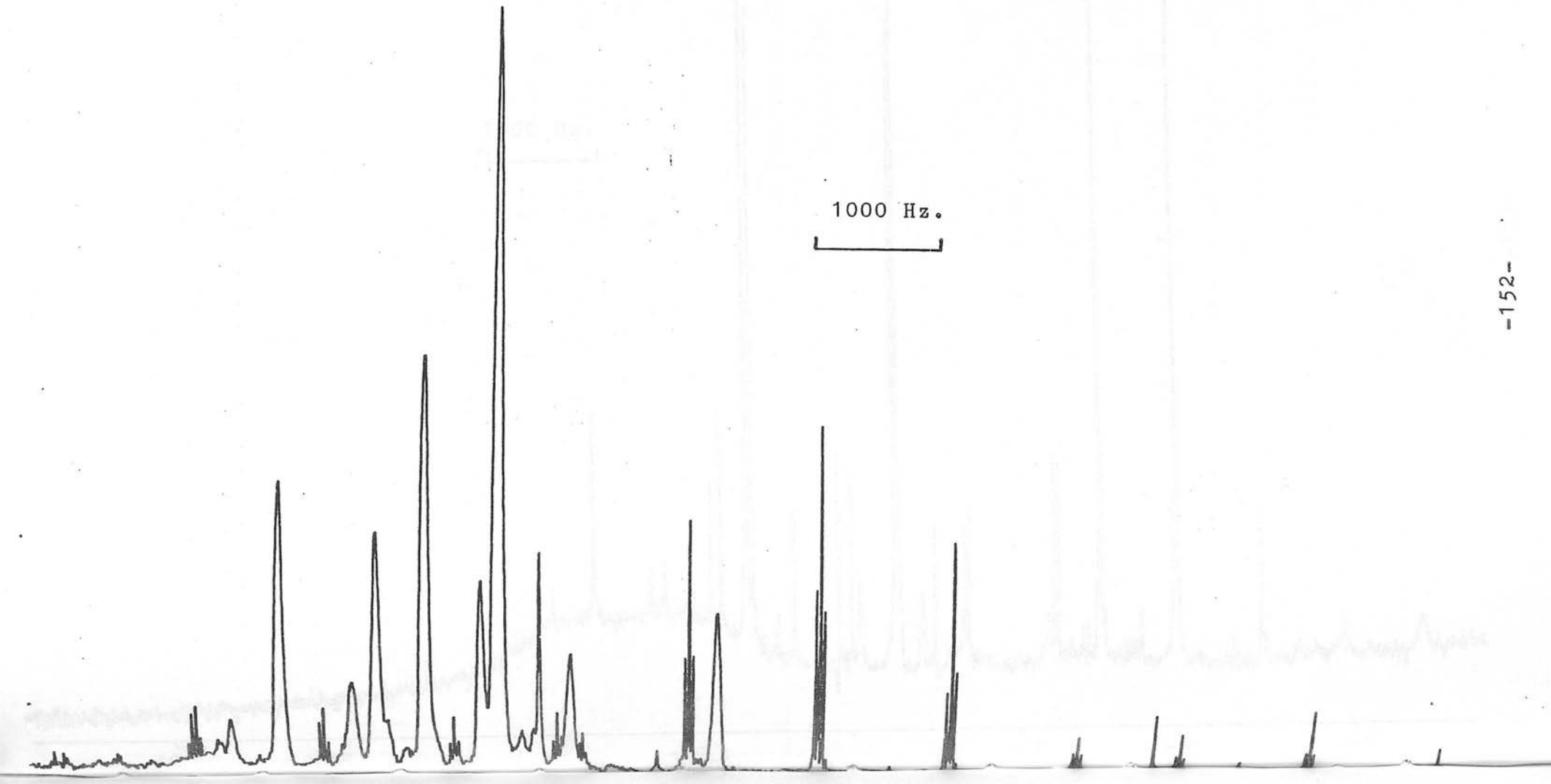
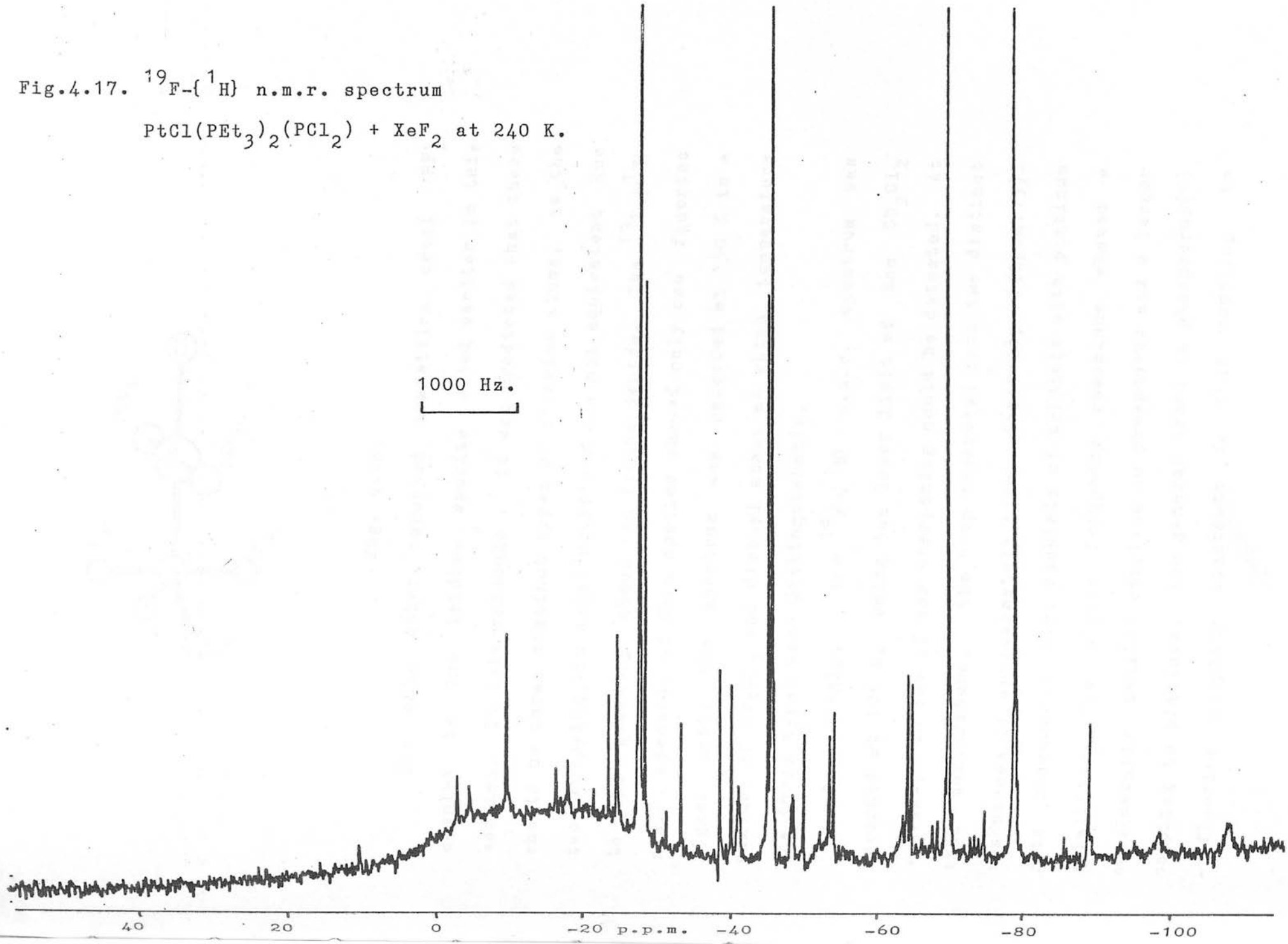


Fig.4.17. $^{19}F-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2)$ + XeF_2 at 240 K.



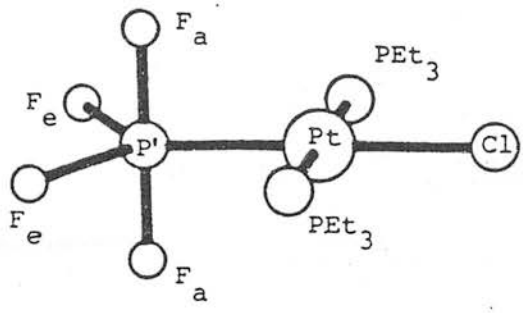


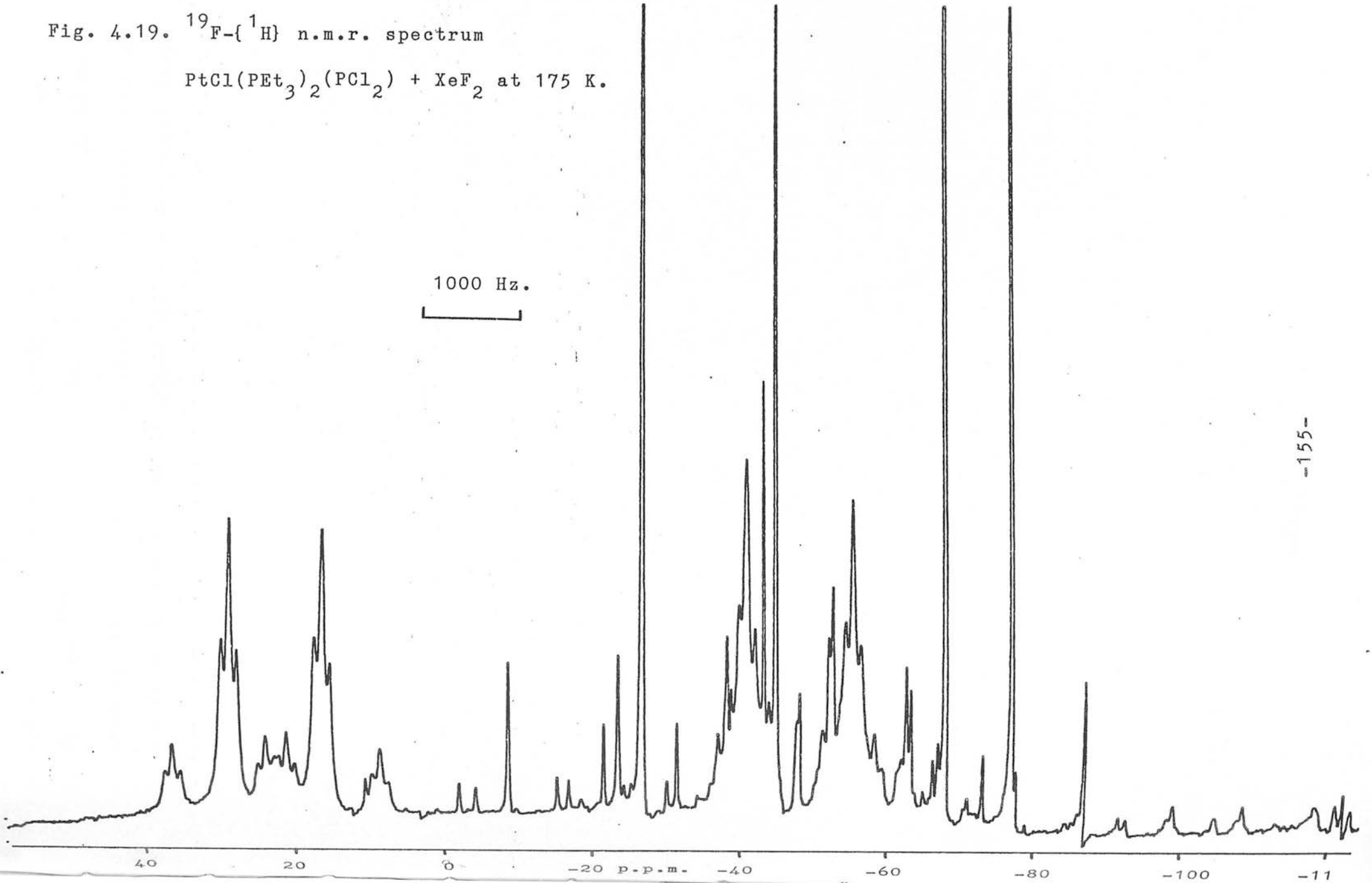
Fig. 4.18.

The only other reported transition metal $-PF_4$ complex is the iridium species cited earlier in this section. In this molecule , it was predicted that there should be three distinct types of fluorine atoms, as the two occupying the axial positions are not equivalent due to the geometry about the irdium centre. The $^{19}F-\{^1H\}$ n.m.r. spectrum of this species showed only one fluorine signal until the spectrum was recorded at 130 K in a mixture of CD_2Cl_2 and diethyl ether at which temperature the three types were distinguishable.

Accordingly, the $^{19}F-\{^1H\}$ n.m.r. spectrum was recorded at 175 K, being the lower limit of the CD_2Cl_2 solvent, to see if any sharpening could be detected. At this temperature, the hump separated into two distinct resonances of approximately equal intensity (fig.4.19). Both resonances were doublets of triplets with platinum satellites. The higher frequency resonance showed a considerably smaller coupling to phosphorus and a larger coupling to platinum. The general trend in phosphorus(V) - fluorine coupling constants is that coupling to

Fig. 4.19. $^{19}F-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2)$ + XeF_2 at 175 K.



equatorial fluorines is larger than that to axial fluorines.[25,26] This may be rationalised in terms of the bonding in a trigonal bipyramid. Phosphorus hybrid orbitals in the equatorial plane may be constructed from a combination of 3s and two 3p orbitals while those on the apical axes from the combination of a 3p and a 3d. This means that a phosphorus-fluorine equatorial bond has a greater degree of s character which results in greater spin transmission and hence a larger coupling constant. The couplings to platinum are also in keeping with established trends. The n.m.r. parameters are detailed below :-

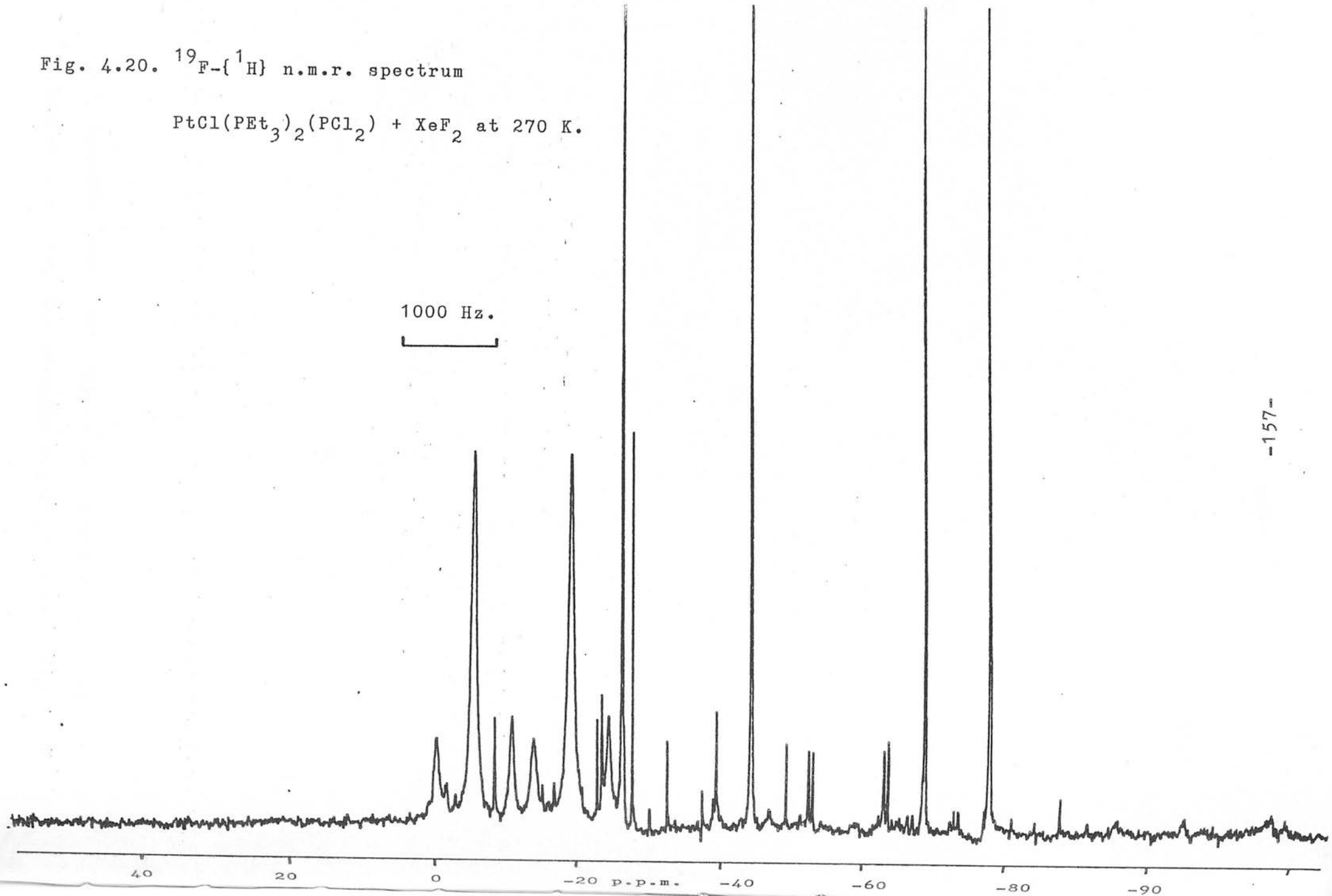
δP = +22.60 p.p.m.	$\delta P'$ = +13.00 p.p.m.
δF_a = +26.41 p.p.m.	δF_e = -46.94 p.p.m.
$^1J_{PtP}$ = 2320 Hz.	$^1J_{PtP'}$ = 7992 Hz.
$^1J_{PF_a}$ = 983 Hz.	$^1J_{PF_e}$ = 1118 Hz.
$^2J_{PP'}$ = 23 Hz.	$^2J_{F_aPt}$ = 1205
$^2J_{F_ePt}$ = 462 Hz.	$^2J_{F_aF_e}$ = 83 Hz.

All parameters were recorded in dichloromethane at 180 K

The $^{19}F-\{^1H\}$ n.m.r. spectrum was then studied as a function of temperature. As the temperature was raised from 180 K, the two resonances broadened and coalesced at about 230 K, giving the spectrum which was initially observed. Further warming resulted in the hump sharpening. At 270 K there was only a single doublet with platinum satellites (fig.4.20). The chemical shift of this doublet was -9.60 compared with the average position of F_a and F_e being -10.20. The coupling to phosphorus was 1054 Hz compared with the average value of

Fig. 4.20. $^{19}F-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2)$ + XeF_2 at 270 K.



1050 Hz. The coupling to platinum was the least accurate at 819 Hz compared with 833 Hz. This suggests that exchange was only marginally slower than the n.m.r. timescale. The lines were still broad at 175 K ($W_{1/2}$ = 60 Hz.) but further warming of the sample resulted in its decomposition before any further spectra could be obtained.

It was apparent from the breadth of the lines that at the low temperature limit of this experiment the distinct fluorine resonances were not completely frozen. It was not deemed to be worth the effort of preparing a sample in a mixed solvent to attain even lower temperatures as no additional information would be gained.

It is worthy of note that in the case of the iridium-PF_4 species that a temperature of 130 K was required to resolve the different environments of the fluorines. In the platinum case, however, the result was obtained at 175 K. This implies that the energy barrier to rotation is lower in the iridium case. No simple explanation can be offered to account for this observation at this time.

4.3. Attempts to dechlorinate $PtCl(PEt_3)_2(PCl_2)$.

Recent work in this department showed that the P-Cl bond of $PCl_2N(CH_3)_2$ added oxidatively to $IrCl(CO)(PEt_3)_2$. Reaction of the six-coordinate product with trityl tetrafluoroborate ($Ph_3C^+ BF_4^-$) produced a species which showed a high frequency resonance at +695 p.p.m. This

was assigned as arising from a cationic species in which the chloride had been removed from the $-PClN(CH_3)_2$ ligand. On this basis it was decided to try to dechlorinate the unique phosphorus of $PtCl(PEt_3)_2(PCl_2)$.

Reaction with (Ph_3C^+ BF_4^-) failed to show any reaction even after standing at 250 K for 8 hours. The reaction was repeated using thallium tetrafluoroborate, again with no detectable reaction. The same occurred using thallium hexafluorophosphate. Reaction with anhydrous aluminium chloride resulted in the rapid decomposition of the $PtCl(PEt_3)_2(PCl_2)$ at 240 K but failed to show any new species. At this juncture it was decided to abandon these reactions.

4.4. Attempts to fluorinate $PtCl(PEt_3)_2(PCl_2)$.

The reaction of PF_2Cl with $Ir(CO)Cl(PEt_3)_2$ produces the species $Ir(CO)Cl_2(PEt_3)_2(PF_2)$.[4] The corresponding reaction with $PtClH(PEt_3)_2$ however produces a binuclear species containing a bridging $-PF_2$ group.[27] The formation of this species is postulated as proceeding via a compound containing a terminal $-PF_2$ group. Various other attempts to prepare a platinum species containing a terminal $-PF_2$ group have met with failure. It was therefore decided to attempt to fluorinate the unique phosphorus of $PtCl(PEt_3)_2(PCl_2)$. This type of fluorination is well known for compounds containing phosphorus chlorine bonds.

e.g. $Cl_2PN(CH_3)_2 + NaF \longrightarrow F_2PN(CH_3)_2$ [28]

Common fluorinating reagents used for this type of

reaction include NaF, CsF, SbF_3 and HgF_2. XeF_2 has also been used as a mild fluorinating agent[21] but the reaction with this have already been discussed in section 4.2.16.

Reaction with an equimolar amount of SbF_3 was studied by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. No reaction was detected until a temperature of 200 K was attained. At this temperature, the $PtCl(PEt_3)_2(PCl_2)$ decomposed very rapidly and the only species remaining were cis and trans $PtCl_2(PEt_3)_2$.

Reactions with NaF, CsF and HgF_2 failed to produce any detectable reaction up to temperatures at which the $PtCl(PEt_3)_2(PCl_2)$ decomposed in the normal manner. This was partly attributed to the insolubility of these reagents in dichloromethane. The solubility of CsF in acetonitrile is quite significant so a sample of $PtCl(PEt_3)_2(PCl_2)$ was prepared in dichloromethane, solvent removed under vacuum and CD_3CN added. Dissolution was allowed to occur before the CsF was added at 77 K. The $^{31}P-\{^1H\}$ n.m.r. spectrum was studied as soon as the solvent had melted at 230 K. The unique phosphorus resonance was very broad and ill defined and remained this way until the sample decomposed at 260 K. No other trace of reaction could be detected. Studying the $^{31}P-\{^1H\}$ n.m.r. spectrum of $PtCl(PEt_3)_2(PCl_2)$ alone in CD_3CN gave identical results to these and it was assumed that the solvent was involved with an exchange process affecting the $-PCl_2$ group.

Reaction with tetramethylammonium fluoride in

dichloromethane resulted in the formation of $PtCl(PEt_3)_2(OPCl_2)$, presumably as a consequence of traces of moisture in the tetramethylammonium fluoride. Rigorous drying of the sample reduced the formation of this species but falied to eliminate it entirely. No other reaction was detected. At this juncture, it was decided to abandon these reactions.

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CHAPTER 5

REACTIONS OF $PtCl(PEt_3)_2(PCl_2)$ WITH TRANSITION METAL SUBSTRATES.

5.1. Introduction.

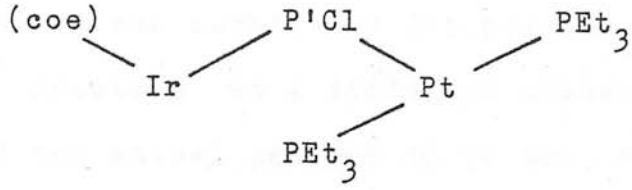
The contents of chapter 4 have illustrated the lability of the $-PCl_2$ group of the title compound in a variety of reactions. Accordingly, it was decided to react it with a range of transition metal substrates in an attempt to produce either hetero- or homo-nuclear binuclear species. There would appear to be two distinct routes by which such a process could occur, firstly, oxidative addition of one of the phosphorus chlorine bonds of the PCl_2 group might occur across the metal centre of a coordinatively unsaturated species. Such a process would generate another three-coordinate phosphorus containing species. This type of reaction was thought most likely to occur with species which exhibit a preference for higher coordination numbers and oxidation states. Secondly, the $-PCl_2$ group could act as a simple donor ligand to form an adduct with the reactant molecule. This process would not involve any change of oxidation state, only of coordination number, at the other metal centre. This process seemed more likely to occur by reaction with binuclear systems containing labile bridging groups which on cleavage would result in two coordinatively deficient centres.

5.2.1. Reaction with $[IrCl(cyclooctene)_2]_2$

The combining ratio for this reaction was one platinum to half an iridium dimer unit. Reaction was detected by $^{31}P-\{^1H\}$ n.m.r. spectroscopy at a temperature

of 190 K when four apparently unrelated singlets were observed in the range +125 ⟶ +70 p.p.m. None of these peaks appeared to have satellites and their chemical shifts did not match those of any known iridium $-PCl_2$ or $-PCl_3$ species. Although they were therefore assumed not to contain a transition metal, their identity remains unknown. Further warming of the sample to 210 K resulted in the disappearence of these resonances and the formation of a very high frequency resonance with platinum satellites centered at +395.10 p.p.m. The lines were rather broad and no structure could be identified. A narrow doublet with platinum satellites, centered at +18.40 p.p.m., was detected at the same time. The coupling to platinum was large at 5640 Hz. and indicated the species contained four-coordinate platinum(II). The high frequency resonance was unaffected by retention of proton coupling and on the basis of its very high frequency shift it was deemed likely that it arose fom a three-coordinate -PCl group bridging between two metal centres. As the platinum satellites were of a normal type and intensity it was assumed that the other metal centre must be an iridium. Further warming the sample to 220 K resulted in the high frequency resonance showing a narrow triplet coupling which matched the doublet coupling in the triethylphosphine resonance. The ^1H nmr spectrum showed the presence of another coordinated cyclooctene molecule in addition to the iridium starting material. The absence of any coupling to phosphorus may tend to suggest that the cyclooctene was in a cis

configuration relative to the bridging phosphorus but the low quality of the spectrum left doubts as to such an asignment. No further information could be obtained as to the structure of the product and it therefore appears that the skeleton is :-



(coe) = cyclooctene

$\delta P = +18.40$ p.p.m. $\quad \delta P' = +395.10$ p.p.m.

$^1J_{PtP} = 5640$ Hz. $\quad ^1J_{PtP'} = 3406$ Hz.

$^2J_{PP'} = 32$ Hz.

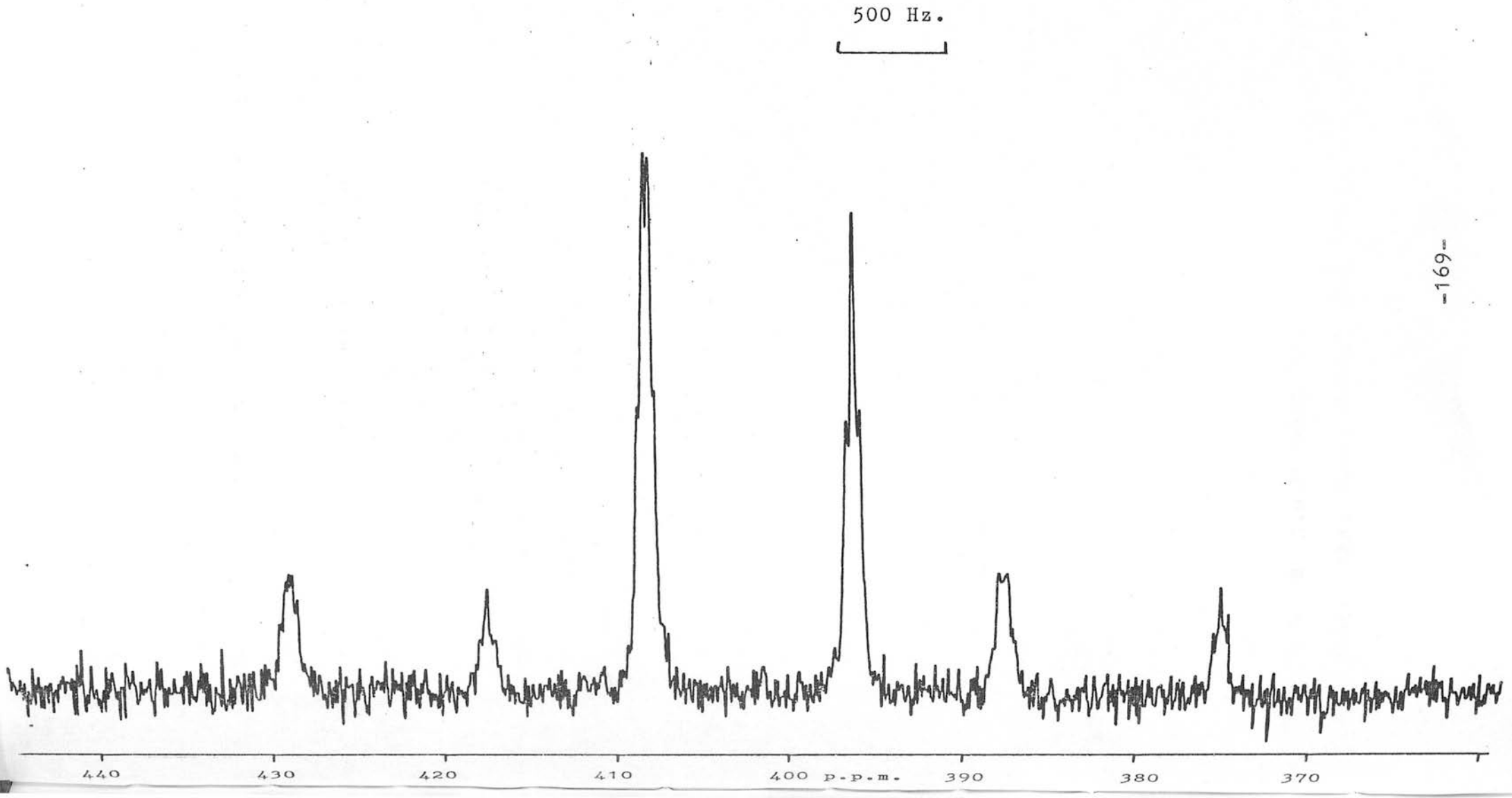
Parameters were recorded in dichloromethane at 220 K

No further proof can be offered as to the remainder of the structure but it seems most likely that the missing ligand on the platinum is chlorine and that the iridium also has one, and probably, two chlorine atoms. As to the coordination number at the iridium centre, with two chlorines, one cyclooctene and a bond to the bridge -PCl, the iridium would be five-coordinate Ir(I). It was not possible to detect free cyclooctene in the proton n.m.r. spectrum but this cannot be taken as proof of its absence due to the number of intense resonances in this part of the spectrum. Alternatively, there may still be two cyclooctenes and a chlorine coordinated to a six-coordinate Ir(III) centre giving rise to a mono-cationic species with the missing chloride present as the counter-anion. Further warming resulted in the formation of another high frequency resonance which

appeared to be a quartet with platinum satellites (fig.5.1). The triethylphosphine region of the spectrum revealed two narrow doublets with platinum satellites centered at +17.44 and +17.97 p.p.m. The intensity of the central high frequency quartet resonance did not appear to be the normal 1:3:3:1 pattern and examination of the spectrum at a different magnetic field strength revealed the actual pattern to be two triplets centered at +405.89 and +406.09 p.p.m. which overlapped at a magnetic field equivalent to 81.02 MHz. The similarity of the n.m.r. parameters for these two species suggests that they are very similar. Although no evidence can be offered to support the suggestion, an explanation can be offered. As the species both contain a -PCl bridge between two different metal centres, the bridge phosphorus is a chiral centre. This allows for different enantiomeric forms. Thus if the second product was a geometric isomer of the first product and there were two enantiomers of this isomer, then the n.m.r. spectrum would be consistent with the observed spectrum. As to the geometry of this isomer, no suggestions are offered at this time other than to suggest it must be very similar to the initial product due to the similarities in their n.m.r. parameters.

Further warming of the sample resulted in the rapid decomposition of all three products and no further new species were observed before the platinum starting material decomposed by the normal route.

Fig.5.1. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + $[IrCl(cyclooctene)_2$ at 230 K.



5.2.2. Reaction with $Ir(CO)Cl(PEt_3)_2$.

Previous studies[1,2] have shown that $Ir(CO)Cl(PEt_2)_2$ readily undergoes oxidative addition with a wide variety of reagents. No reactions of this molecule have resulted in the formation of a five-coordinate Ir(I) species. It was therefore hoped that reaction with $PtCl(PEt_3)_2(PCl_2)$ would occur via oxidative addition across one of the phosphorus chlorine bonds. Unlike the previous reaction, the presence of spinning nuclei on the iridium centre should give a "handle" as to the coordination at iridium.

Reaction was detected by the $^{31}P-\{^1H\}$ n.m.r. spectrum as soon as the solvent melted. A new high frequency narrow triplet was observed centered at +304.00 p.p.m. and a corresponding doublet centered at -9.21 p.p.m., neither of which showed platinum satellites. From the n.m.r. parameters, the product was identified as $IrCl_2(CO)(PEt_3)_2(P'Cl_2)$. No resonance attributable to excess PCl_3 was detected. Further warming the sample to 180 K resulted in an increase in the concentration of this product which suggests that it is derived from exchange with the $PtCl(PEt_3)_2(PCl_2)$ rather than from reaction with excess PCl_3 . The mechanism for the formation of this species is not simple as loss of PCl_3 from $PtCl(PEt_3)_2(PCl_2)$ is required. This loss would leave a strange platinum species containing only two triethyl phosphine groups. Close examination of the $^{31}P-\ ^1H$ n.m.r. spectrum failed to reveal any resonances other than those already described. Removal of the tube

from the probe of the spectrometer showed the solution to be turbid. No simple explanation can be proposed at this time.

Warming the sample to 210 K resulted in a further new set of resonances forming. In the high frequency region, a wide triplet of narrow triplets with platinum satellites was centered at +413.22 p.p.m. (fig.5.2.) Once again, this is the region associated with a bridging -PCl group. Retention of proton coupling had no effect on this set of resonances. The triethylphosphine region of the $^{31}P-\{^{1}H\}$ n.m.r. spectrum (fig.5.3.) showed two new sets of resonances. The first of which was a narrow doublet of triplets with platinum satellites. The magnitude of the coupling to platinum showed the species to contain four-coordinate platinum(II). The doublet coupling matched the narrow triplet coupling in the high frequency resonance. The second resonance was a wide doublet of triplets with what appeared to be platinum satellites bordering on the main resonances. The doublet coupling in this resonance matched the wide triplet coupling in the high frequency resonance. The very small coupling to platinum shows that the platinum is not directly bonded to these triethylphosphines but is in the same molecule. The chemical shift of the triethylphosphine resonance is suggestive of a six-coordinate iridium(III) species. The ^{1}H nmr spectrum failed to show a low frequency hydride. These observations suggest that the product consists of a four-coordinate platinum(II) centre containing two

Fig. 5.2. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + $IrCOCl(PEt_3)_2$ at 210 K.

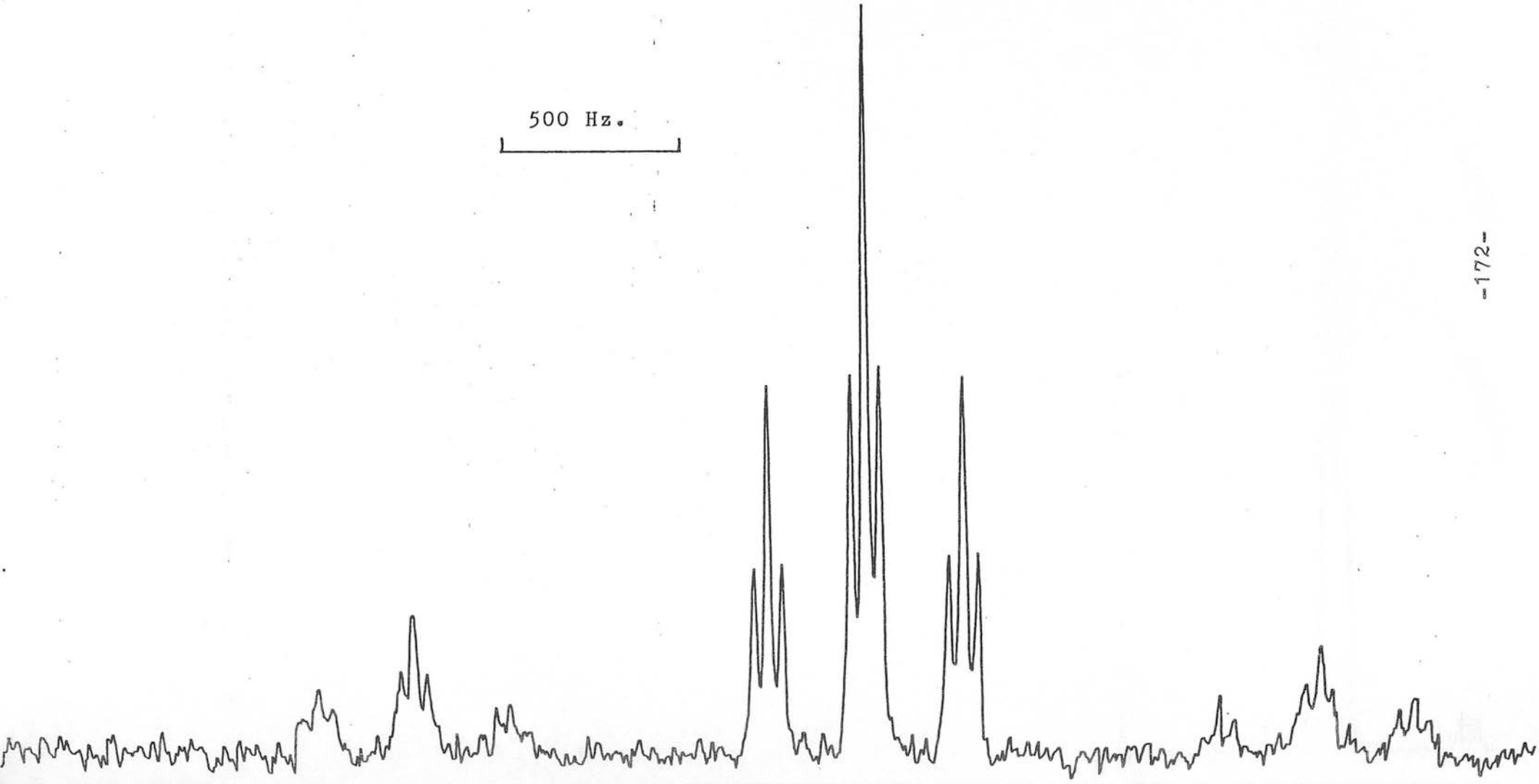
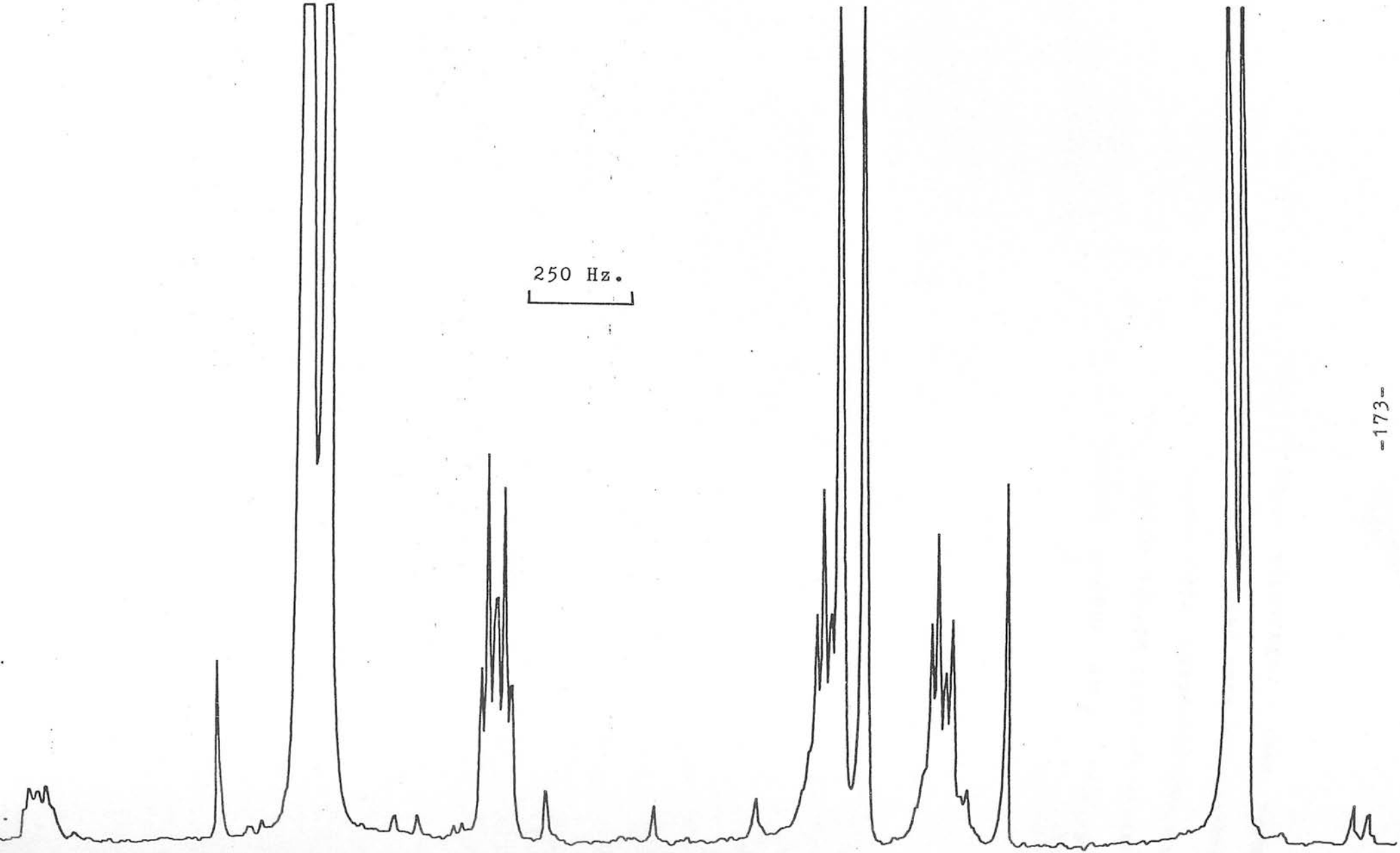
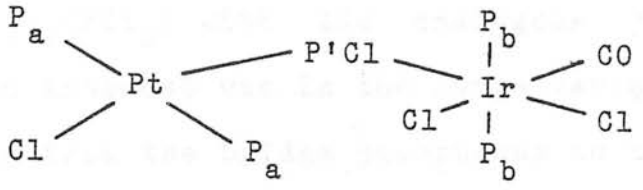


Fig. 5.3. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + $IrCOCl(PEt_3)_2$ at 210 K.



triethylphosphines linked to a six-coordinate iridium(III) centre, also containing two triethylphosphines, via a -PCl bridge. It again seems reasonable to assume that the fourth coordination site on the platinum is still occupied by a chloride. If it is assumed that the reaction has proceeded by oxidative addition of a phosphorus-chlorine bond across the iridium centre, then the three remaining coordination sites on the iridium are occupied by a carbonyl and two chlorides. The problem then arises as to whether a chlorine or the carbonyl is in the position trans to the bridge phosphorus. If it was the carbonyl, then the $^{13}C\{^{1}H\}$ n.m.r. spectrum would hopefully show a significant coupling to the phosphorus of the bridge. It was thought unlikely that such a coupling would be detected if the carbonyl was cis to the bridge. Attempts to obtain a good enough quality $^{13}C\{^{1}H\}$ n.m.r. spectrum failed when conventional techniques were used due to the relatively low concentration of the product and the inability to accumulate the spectrum overnight due to hardware limitations. Accordingly the pulse sequence QUATGEN[3] was used. Unlike the DEPT sequence previously described, this sequence does not use a sensitivity enhancement technique, but merely shows only the quaternary carbons. This enables the spectrum to be run over very narrow spectral widths without the problems of intense triethylphosphine resonances folding back. The longer acquisition time required for a narrow spectral width means that a relaxation delay is effectively inbuilt and

the accumulation is much more time efficient. The resultant spectrum failed to show any coupling to phosphorus and on this basis the carbonyl was assumed to be cis to the bridge. Thus the structure of the product was assigned as



(P_a & P_b = PEt_3.)

δP_a = +14.93 p.p.m. δP_b = +3.30 p.p.m.

$\delta P'$ = +413.21 p.p.m. $^1J_{PtP_a}$ = 2288 Hz.

$^1J_{PtP'}$ = 2603 Hz. $^2J_{P_a P'}$ = 41 Hz.

$^2J_{P_b P'}$ = 280 Hz. $^3J_{PtP_b}$ = 72 Hz.

$^4J_{P_a P_b}$ = 15 Hz.

All parameters were recorded in dichloromethane at 210 K.

The difference in the values of the two-bond couplings of the bridging phosphorus to the two different sets of triethylphosphines is surprisingly large (280 vs. 41 Hz.). No explanation can be offered at this time but the difference is certainly worthy of note.

Further warming of the sample above 210 K resulted in the decomposition of this species leaving an approximately 1:1 mixture of $PtCl(PEt_3)_2(PCl_2)$ and $Ir(CO)Cl_2(PEt_3)_2(PCl_2)$. The relative amounts of these compounds did not alter until ambient temperature was reached and the platinum species started to decompose. No further new species were detected in the course of

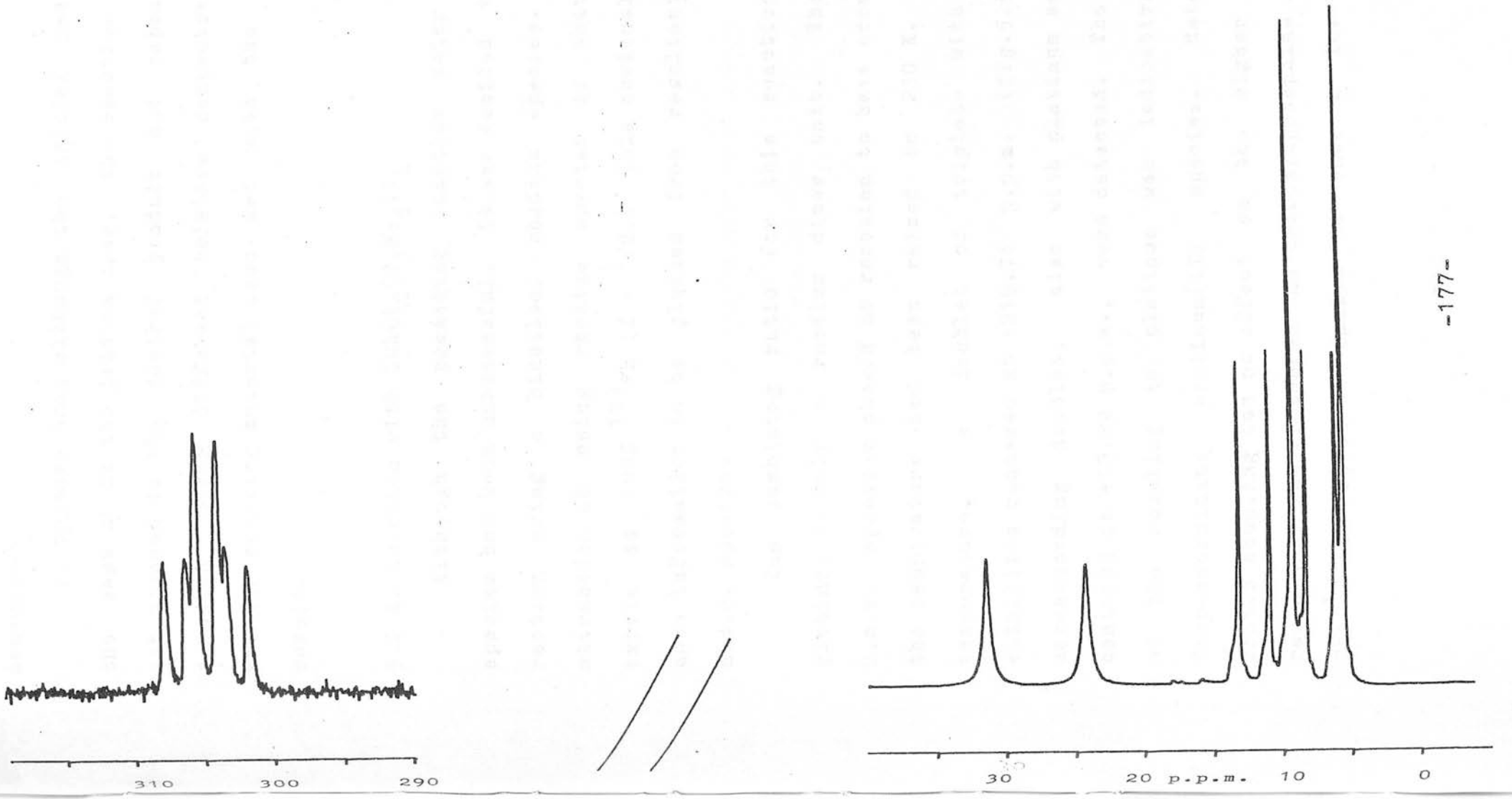
warming to ambient temperature.

5.2.3. Reaction with $Rh(CO)Cl(PEt_3)_2$

In view of the novel species obtained in the preceding section, it was decided to try the reaction of $PtCl(PEt_3)_2(PCl_2)$ with the analogous rhodium species. The main interest was in the large variation between the couplings from the bridge phosphorus to the two different sets of triethylphosphines.

Reaction was rapid and as soon as the solvent had melted the $^{31}P-\{^1H\}$ n.m.r. spectrum showed resonances which were attributed to the two starting materials and two new sets of resonances. The first of these was a triplet of doublets just to high frequency of the unique phosphorus resonance of $PtCl(PEt_3)_2(PCl_2)$. The other resonance was a doublet of doublets in the triethylphosphine region. Neither set of resonances had platinum satellites and the species was identified as being $Rh(CO)Cl_2(PEt_3)_2(PCl_2)$ on the basis of its n.m.r. parameters from previous work.[2] This behaviour is analogous to the first stage of the reaction with the iridium analogue. Once again no simple mechanism can be postulated for this reaction. Further warming of the sample to 210 K resulted in an increase in the relative concentration of $Rh(CO)Cl_2(PEt_3)_2(PCl_2)$. Further warming above this temperature had no effect on the relative concentrations of the species present (fig.5.4) and at ambient temperatures the two $-PCl_2$ species started to

Fig. 5.4. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + $RhCOCl(PEt_3)_2$ at 230 K.



decompose.

It appears that although the initial reaction is the same as in the iridium case, the reaction then does not proceed to the desired product and repeating the reaction using different relative concentrations of rhodium starting material also met with the same net result.

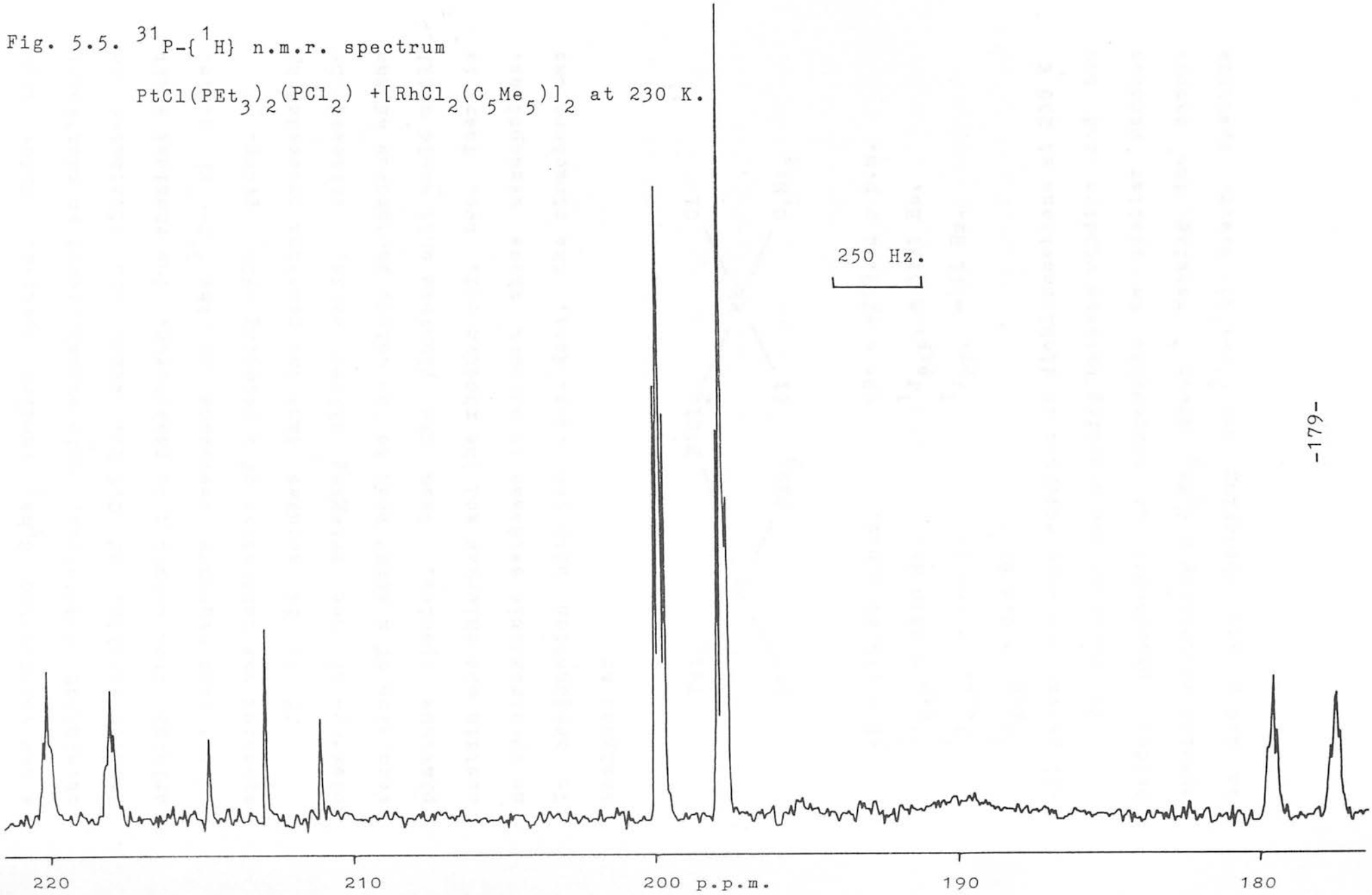
5.2.4. Reaction with $[RhCl_2(C_5Me_5)]_2$

Although the preceding reaction using a rhodium species had been unsucessful, it was decided to try a rection using a binuclear rhodium species. The main attraction of using rhodium species is that rhodium exists as 100% ^{103}Rh ($I = {}^1/_2$.) This obviously enables more information to be gleaned from resultant $^{31}P-\{^1H\}$ n.m.r. spectra.

The combining ratio for this reaction was one platinum to half a rhodium dimer unit. The $^{31}P-\{^1H\}$ n.m.r. spectrum showed no reaction to have occured until the temperature had been raised to 230 K. At this temperature, a doublet of triplets with platinum satellites centered at +219.74 p.p.m. (fig.5.5) and a corresponding doublet, also with platinum satellites, centered at +19.89 p.p.m., were detected. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. Retention of proton coupling had no effect on the higher frequency resonance but broadened the triethylphosphine resonance. The ^1H nmr spectrum failed to show a low frequency

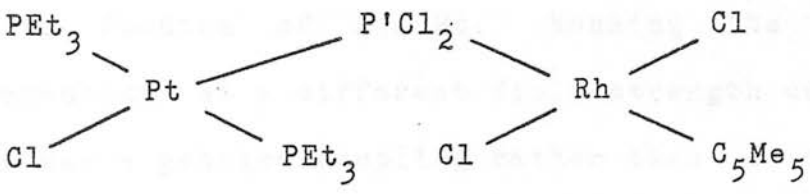
Fig. 5.5. $^{31}P-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2)$ +$[RhCl_2(C_5Me_5)]_2$ at 230 K.



hydride signal but did show a resonance corresponding to a new coordinated C_5Me_5 rhodium species. Under high resolution conditions, this signal showed an additional doublet coupling of 0.8 Hz. which was attributed as arising from coupling to phosphorus. The chemical shift of the high requency resonance in the $^{31}P-\{^1H\}$ n.m.r. spectrum was indicative of a bridging $-PCl_2$ group.

If it is assumed that the reaction proceeded by cleavage of the bridging chloro bonds, followed by formation of a donor bond to the unique phosphorus of the platinum species, then the platinum unit would still contain one chlorine and the rhodium end, two. There is no spectroscopic evidence to support these assumptions. In conjunction with the n.m.r. data, the structure was assigned as



$\delta P = +19.89$ p.p.m. $\quad \delta P' = +219.74$ p.p.m.

$^1J_{PtP} = 2810$ Hz. $\quad ^1J_{PtP'} = 3271$ Hz.

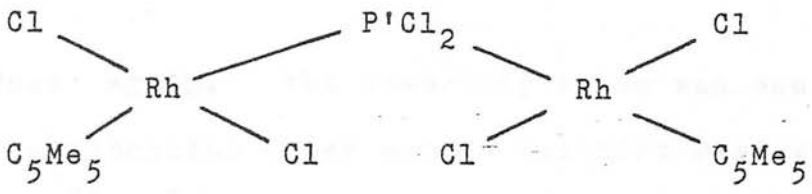
$^1J_{RhP'} = 166$ Hz. $\quad ^2J_{PP'} = 12$ Hz.

$^3J_{RhH} = 0.8$ Hz.

All parameters were recorded in dichloromethane at 230 K

The value of the coupling between rhodium and the bridge phosphorus is comparable to similar rhodium species containing a C_5Me_5 group.[4] Warming the sample to 240 K and observing the $^{31}P-\{^1H\}$ n.m.r. spectrum

showed a further product to have formed. In the high frequency region, a triplet of coupling 171 Hz. and a doublet of coupling 244 Hz. were observed. Neither of these resonances showed platinum satellites. The chemical shifts were indicatve of bridging $-PCl_2$ groups. The ^1H nmr spectrum showed the presence of at least two, and probably three or more, new coordinated C_5Me_5 groups. The triplet resonance showed no change upon retention of proton coupling. Although speculative, the species was assigned as being



The doublet resonance had an exceptionally large coupling to rhodium of 244 Hz. Running the $^{31}P-^1H$ n.m.r. spectrum at a different field strength confirmed that this was a genuine coupling rather than a chemical shift difference. Retention of proton coupling split each of the lines into a symmetrical ten-line pattern which was of a complex nature, possibly second order. No further information could be obtained regarding the identity of this species and further work will have to be carried out at some later date.

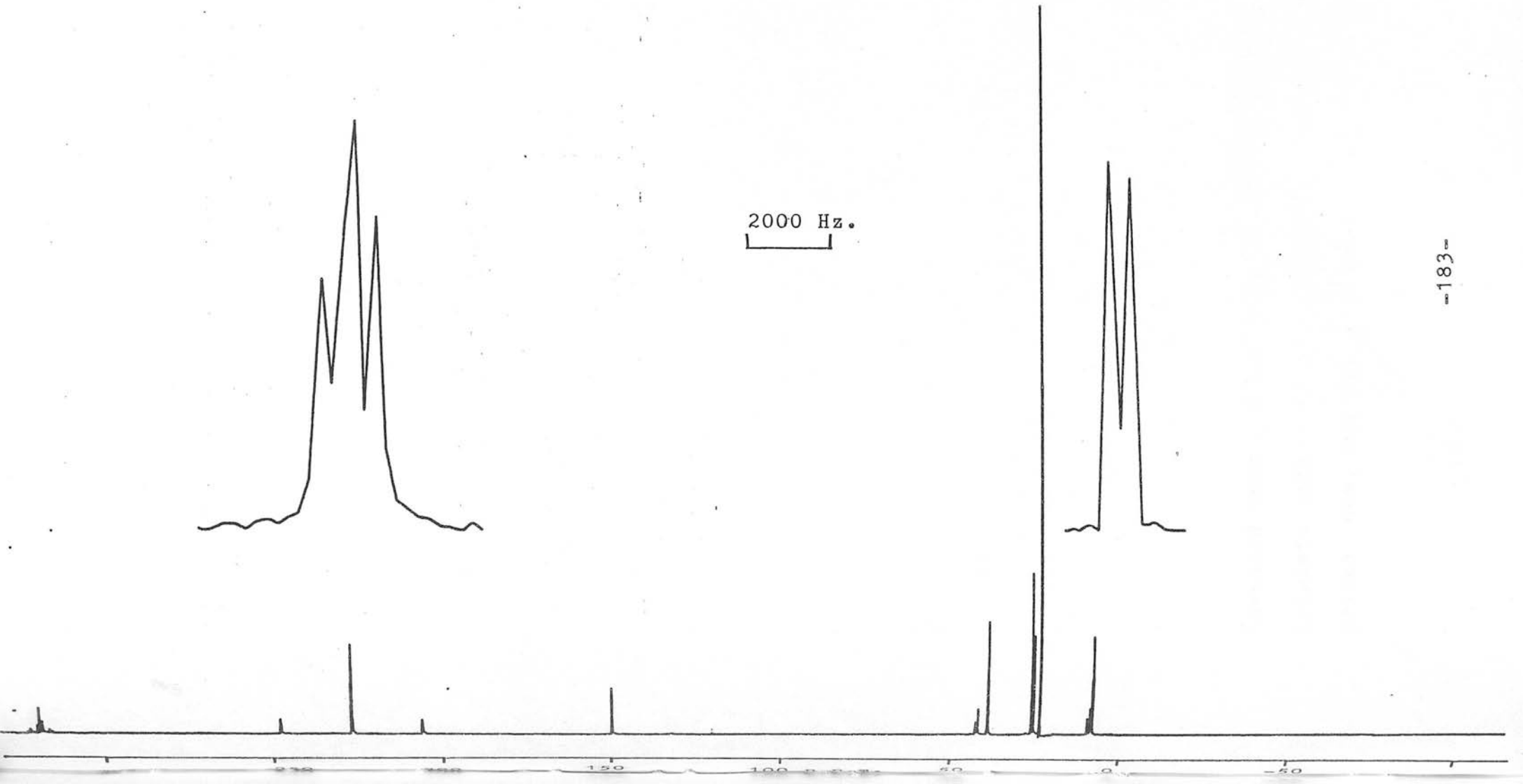
Further warming of the sample resulted in the $^{31}P-\{^1H\}$ n.m.r. spectrum showing three new resonances in the PCl_3 region with doublet ^{103}Rh couplings. The ^1H nmr spectrum was now too complex in the region

associated with coordinated C_5Me_5 to allow interpretation. The species were present in very low concentrations and warming the sample to 250 K in an attempt to increase their concentration resulted in the decomposition of all of these species. No further new products were detected on further warming and the $PtCl(PEt_3)_2(PCl_2)$ decomposed as the temperature reached ambient. Obviously, more work is required on this system when time permits.

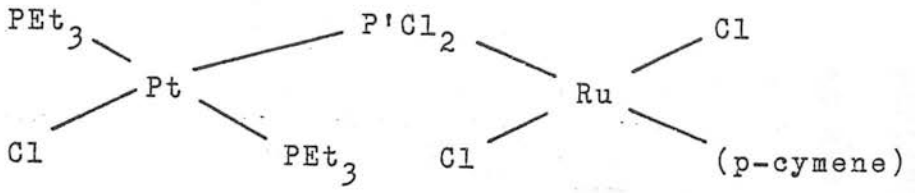
5.2.5. Reaction with $[RuCl_2(p\text{-cymene})]_2$

Once again, the combining ratio was one platinum to half a ruthenium dimer unit. Reaction was very slow and the $^{31}P-\{^1H\}$ n.m.r. spectrum did not show any reaction until the temperature was raised to 230 K. (fig.5.6) A narrow doublet with platinum satellites was centered at +18.10 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. In the high frequency region a corresponding narrow triplet, also with platinum satellites, was centered at +221.09 p.p.m. This chemical shift is, once again, indicative of a bridging $-PCl_2$ group. The ^1H nmr spectrum showed the presence of a resonance corresponding to a new coordinated p-cymene group but due to the breadth of the resonance it was not possible to ascertain whether a phosphorus coupling was also present. On the assumption that the reaction has proceeded by the same route as those already described,

Fig. 5.6. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + $[RuCl_2(p\text{-cymene})]_2$ at 230 K.



the structure is most likely to be



-or an isomer thereof.

$\delta P = +18.10$ p.p.m. $\quad \delta P' = +221.09$ p.p.m.

$^1J_{PtP} = 2504$ Hz. $\quad ^1J_{PtP'} = 3372$ Hz.

$^2J_{PP'} = 14$ Hz.

All parameters were recorded in dichloromethane at 230 K

This product remained stable to 270 K above which both it and the residual $PtCl(PEt_3)_2(PCl_2)$ decomposed. No other new products were detected.

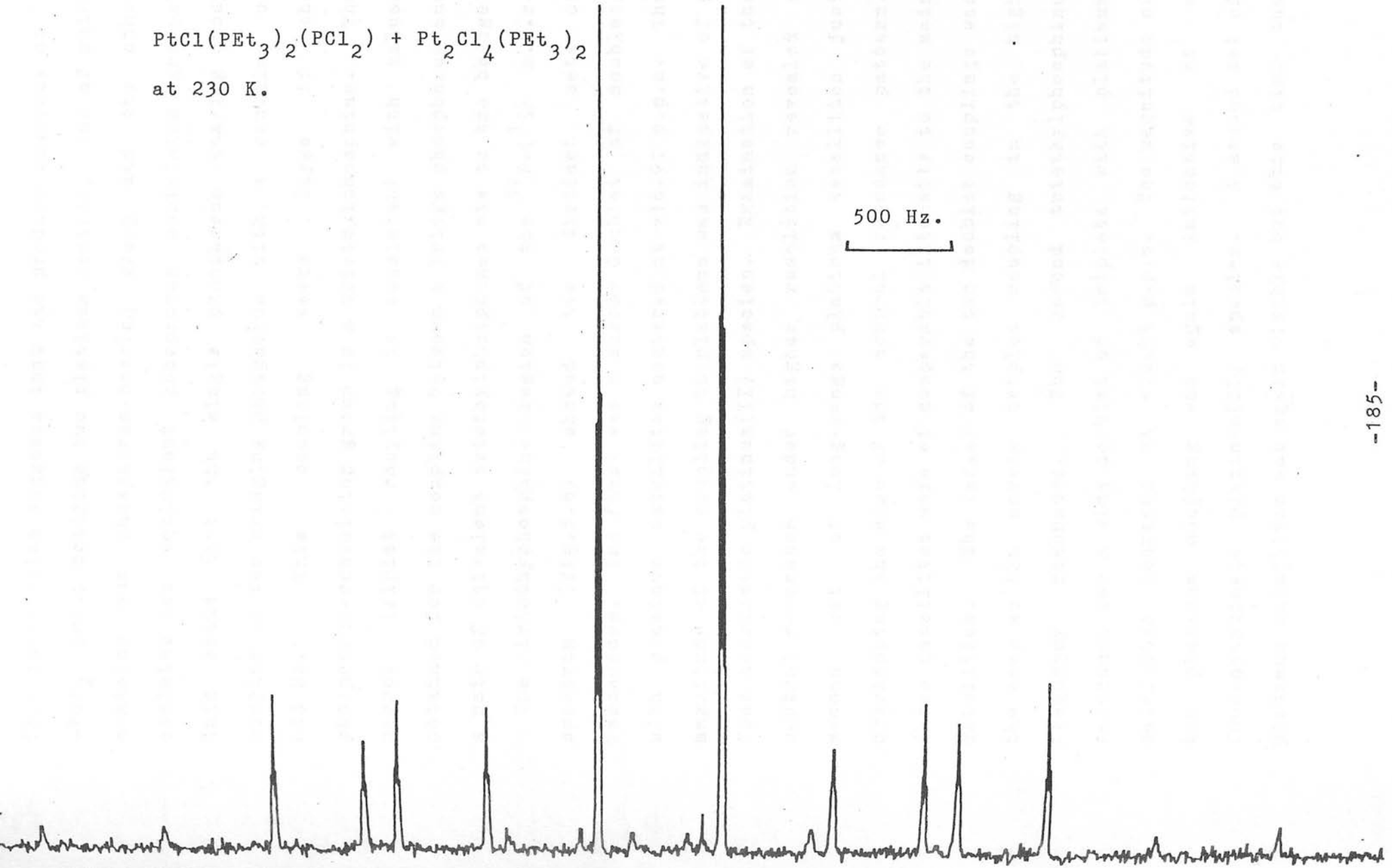
5.2.6. Reaction with $Pt_2Cl_4(PEt_3)_2$.

Once again, the combining ratio was one $PtCl(PEt_3)_2(PCl_2)$ to half a binuclear platinum unit. Reaction was slow and the $^{31}P-\{^1H\}$ n.m.r. spectrum failed to show any reaction until the temperature was raised to 230 K. The high frequency end of the spectrum, in the region normally associated with bridging $-PCl_2$ groups, showed a novel pattern (fig.5.7). What appeared to be two sharp, narrow triplets of equal intensity, separated by 608 Hz, each of which apparently possesed two sets of platinum satellites. Rerunning the spectrum at a lower magnetic field corresponding to 24.21 MHz., revealed that the two triplets were actually a doublet of triplets separated by a coupling of 608 Hz. Retention of proton coupling had no effect on this set of resonances.

Fig.5.7. $^{31}P-\{^{1}H\}$ n.m.r. spectrum

$PtCl(PEt_3)_2(PCl_2) + Pt_2Cl_4(PEt_3)_2$

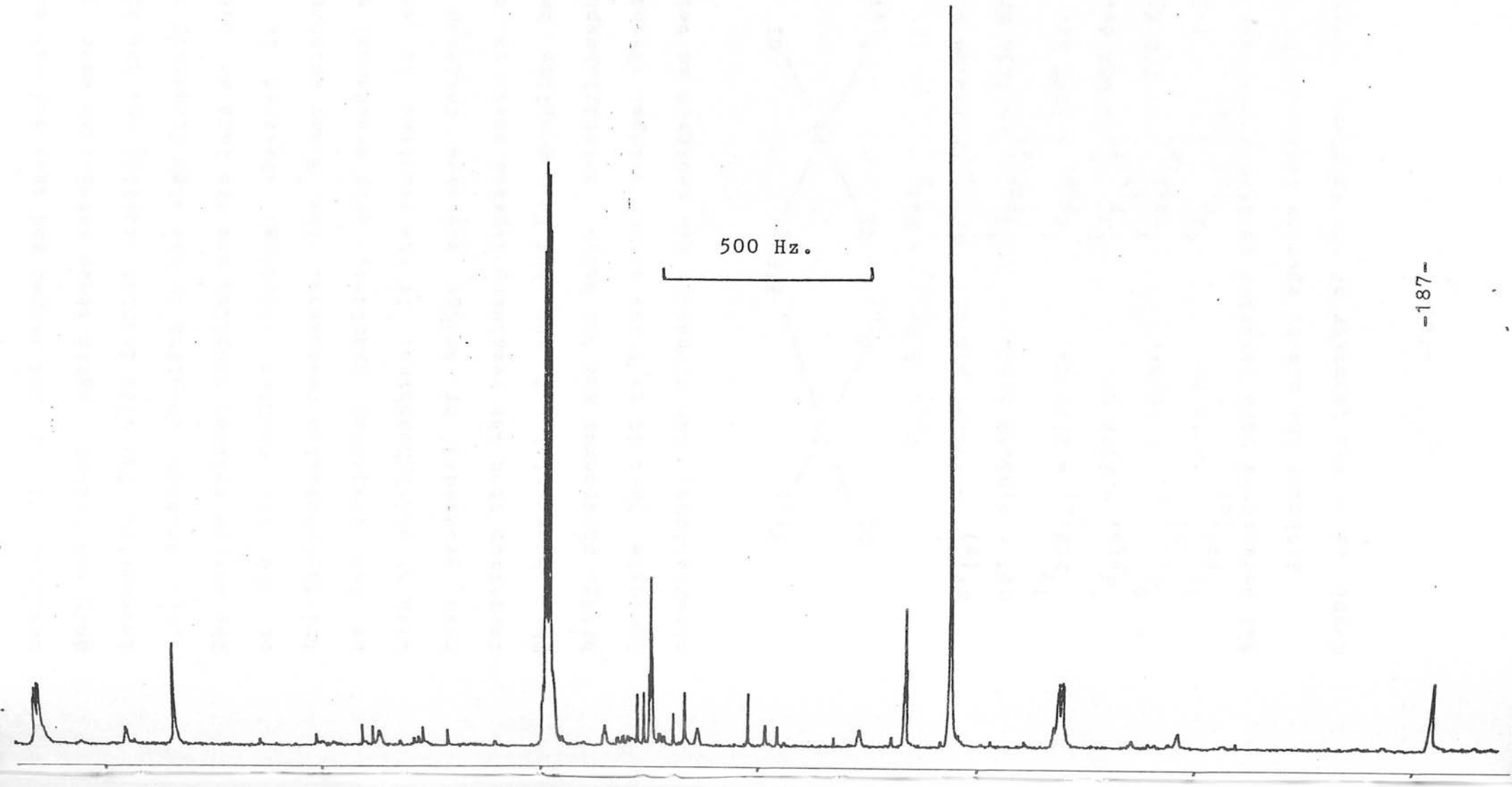
at 230 K.



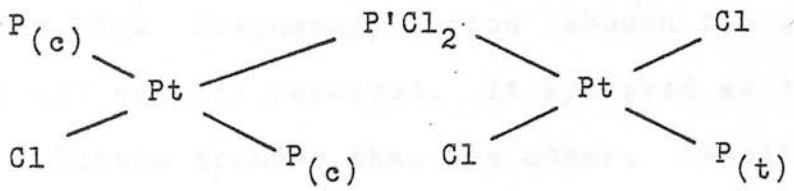
This information suggests that the product consists of a $-PCl_2$ group bridging two platinum centres, one of which contains one phosphorus-bearing group and the other contains two equivalent phosphorus containing groups. This means that the single phosphorus bearing group couples to the bridging phosphorus with a coupling of 608 Hz. This coupling seems large if the phosphorus-containing group is a triethylphosphine. The narrow triplet coupling is consistent with values obtained for the coupling between a bridge phosphorus and a pair of eqivalent triethylphosphines cis to the bridge.

The triethyphosphine region of the $^{31}P-\{^{1}H\}$ n.m.r. spectrum (fig.5.8) showed two distinct sets of resonances. The first was a narrow doublet of doublets with platinum satellites centered at +16.91 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. Examination of the central resonance under higher resolution revealed a second set of long-range platinum satellites just overlapping the edge of the central resonance pattern. These satellites were of comparable intensity to the main satellites. The larger of the two doublet couplings was the same as the narrow triplet coupling in the high frequency resonance. The second triethylphosphine resonance was a wide doublet of triplets with platinum satellites centered at +10.08 p.p.m. The magnitude of the platinum coupling was again indicative of a four-coordinate platinum(II) species. A second set of platinum satellites was again visible but this time the

Fig. 5.8. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtCl(PEt_3)_2(PCl_2)$ + $Pt_2Cl_4(PEt_3)_2$ at 230 K.



coupling was a lot larger and they did not overlap the main resonances. Again these satellites were of normal intensity. The wide doublet coupling was the same as the large doublet coupling in the high frequency resonance. The narrow triplet coupling was the same as the smaller of the two doublet couplings observed in the other triethylphosphine resonance. The ^{1}H nmr spectrum showed no low frequency hydrides, only resonances associated with triethylphosphine. If the reaction is assumed to have proceeded by bridge cleavage followed by donor formation then the remaining ligands must be chlorines. The observation of the 608 Hz. coupling between the bridge phosphorus and the unique triethylphosphine must indicate that it is trans to the bridge. Based on these observations, the structure was assigned as being



$P_{(c)}$ & $P_{(t)}$ = PEt_3

$\delta P_{(c)}$ = +16.91 p.p.m.	$\delta P_{(t)}$ = +10.08 p.p.m.
$\delta P'$ = +196.69 p.p.m.	$^{1}J_{PtP_{(c)}}$ = 2454 Hz.
$^{1}J_{PtP_{(t)}}$ = 2536 Hz.	$^{1}J_{PtP'}$ = 3197 Hz.
$^{1}J_{PtP'}$ = 2312 Hz.	$^{2}J_{P_{(t)}P'}$ = 608 Hz.
$^{2}J_{P_{(c)}P'}$ = 10 Hz.	$^{3}J_{PtP_{(c)}}$ = 222 Hz.
$^{3}J_{PtP_{(c)}}$ = 13 Hz.	$^{4}J_{P_{(c)}P_{(t)}}$ = 3.5 Hz.

All parameters were recorded in dichloromethane at 230 K

Although the n.m.r. spectra leave little room for doubt as to the identity of the species, there are some

points worthy of note regarding some of the parameters. The value of the coupling between the bridge phosphorus and the unique triethylphosphine is exceptionally large. Although none of the other compounds in this work has an analogous coupling with which to compare it, it does seem large for a two- bond coupling. The value of the coupling between the bridge phosphorus and the pair of cis triethylphosphines is very much smaller than the comparable coupling in the platinum-iridium bridged species obtained in section 5.2.2. The variation in the three-bond couplings of the triethylphosphines to platinum is also substantial but three bond couplings are known to be very sensitive to the dihedral angle separating the nuclei. The difference in the couplings to the two different platinums of the bridge phosphorus is not surprising considering the different trans ligands.

The high frequency region showed the satellites were not all equally resolved. It appeared as though one set was a little broader than the other, resulting in an apparent loss of resolution. In an attempt to establish if this effect was genuine, the spectrum was recorded at a higher magnetic field corresponding to 145.79 MHz. This resulted in all of the satellites in the high frequency region becoming broad and failing to show any structure whatsoever. When the spectrum was observed at a lower magnetic field corresponding to 24.21 MHz., all the satellites were sharp and well resolved. This effect was attributed to an enhanced rate of relaxation by Chemical Shift Anisotropy (C.S.A.).[5] It is known that

for heavy nuclei such as ^{195}Pt, C.S.A. is more dominant at higher magnetic fields. C.S.A. is the dominant relaxation mechanism in less symmetric environments while spin rotation relaxation dominates in more symmetric environments.[6] It would appear therefore, that at the observing field equivalent to 81.02 MHz., the satellites which are broadened arise from coupling to the less symmetrical end of the molecule. Although both ends appear to be of approximately similar symmetry, presumably there is enough distortion present to allow this effect to manifest itself.

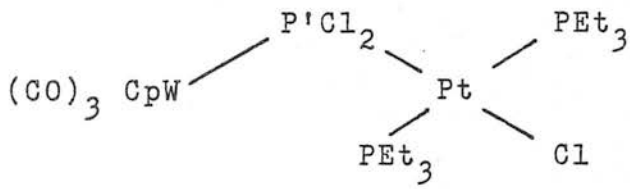
This product remained stable up to 260 K and decomposed to a variety of products if warmed further.

5.2.7. Reaction with $[W(CO)_3(C_5H_5)]_2$

The combining ratio was again one platinum to half a tungsten dimer unit. Reaction was rapid and as soon as the solvent melted, the $^{31}P-\{^1H\}$ n.m.r. spectrum showed the presence of two new species. A narrow doublet with platinum satellites was centered at +22.15 p.p.m. and a corresponding narrow triplet, also with platinum satellites, was centered at +194.09 p.p.m. The coupling to platinum of the triethylphosphine signal was indicative of a four-coordinate platinum(II) species. Retention of proton coupling had no effect on the high frequency resonance and broadened the triethylphosphine resonance as usual. The chemical shift of the unique phosphorus resonance was suggestive of a bridging $-PCl_2$

species. As the platinum satellites were of normal intensity and disribution, it seemed likely that the other metal centre was tungsten. Observing the unique phosphorus under conditions of high resolution and line narrowing the F.I.D. prior to transformation showed rather broad ^{183}W satellites (^{183}W - 14.4%, I = $^{1}/2$) The coupling of 82 Hz. is within the normal range for a one bond phosphorus tungsten coupling.[7,8] The breadth of the satellite lines was presumed to be a consequence of an enhanced rate of relaxation caused by Chemical Shift Anisotropy as discussed in the previous section.

The ^{1}H nmr spectrum showed a resonance assigned to a new coordinated cyclopentadiene group. The lines were too broad to ascertain whether a phosphorus coupling was present or not. Assuming that the normal mode of reaction has occured, the product was asigned the structure



Spectra were recorded in dichloromethane at 180 K

δP = +22.15 p.p.m.	$\delta P'$ = 194.08 p.p.m.
$^{1}J_{PtP}$ = 2488 Hz.	$^{1}J_{PtP'}$ = 2985 Hz.
$^{2}J_{PP'}$ = 30 Hz.	$^{1}J_{WP'}$ = 82 Hz.

Further warming the sample resulted in the decomposition of this species and the formation of a sharp singlet with ^{183}W satellites at +134.04 p.p.m. in the $^{31}P\{^{1}H\}$ n.m.r. spectrum. The chemical shift is suggestive of a coordinated PCl_3 group. The coupling to

tungsten was 60 Hz. Retention of proton coupling led to a slight broadening of the signal but no further coupling could be resolved. Further warming resulted in the decomposition of this species and no further products were detected before the $PtCl(PEt_3)_2(PCl_2)$ decomposed at ambient temperatures. To gain more information about the second species formed would necessitate obtaining a ^{183}W spectrum and the facilities for this were not available in this department.

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CHAPTER 6.

REACTIONS OF $PtH_2(PCy_3)_2$ WITH DIFLUOROPHOSPHINE SPECIES.

6.1. Introduction.

The reactions reported in chapters 4 and 5 of this work have illustrated the wide variety of reactions which $PtCl(PEt_3)_2(PCl_2)$ can undergo. The synthesis of this species was undertaken because of the wide range of reactions observed for the analogous iridium(III) species $Ir(CO)Cl_2(PEt_3)_2(PX_2)$. Compounds where X = Cl and X = F have been prepared and and isolated as thermally stable products.[1,2] Although the preparation of $PtCl(PEt_3)_2(PCl_2)$ has been described in chapter 2 of this work, the corresponding species containing the terminal $-PF_2$ group has never been detected, much less isolated. The synthesis of such a species is obviously highly desirable, as a study of its reactions would be greatly simplified by the presence of the fluorines on the unique phosphorus, which would render the interpretation of the resultant n.m.r. spectra a much simpler task than in the case of the $-PCl_2$ species.

Reaction of $PtCl(PEt_3)_2(PCl_2)$ with xenon difluoride resulted in the production of the $-PF_4$ species described in chapter 4. Other attempts to fluorinate the unique phosphorus without oxidation also met with failure. $Ir(CO)Cl_2(PEt_3)_2(PF_2)$ is prepared by the reaction of PF_2Cl with $IrCl(CO)(PEt_3)_2$. Reaction[3] of PF_2Cl with $PtClH(PEt_3)_2$ however, results in the formation of the $-PF_2$ bridged species $Cl(PEt_3)_2Pt(P^tF_2)Pt(PEt_3)_2Cl$. The proposed mechanism for the formation of this species is by initial oxidative addition to yield a six-coordinate

platinum(IV) species containing a terminal $-PF_2$ group which rapidly eliminates HCl reductively to leave the desired four-coordinate platinum(II)-PF_2 species. The HCl then protonates the $-PF_2$ group and the resulting complex reacts with unreacted starting material resulting in the final $-PF_2$ bridged species. At no stage in the study of this reaction were either of the species containing a terminal $-PF_2$ group observed.

In a further attempt to synthesise, or at least to observe, a species containing a terminal $-PF_2$ group, it was decided to study the reactions of $PtH_2(PCy_3)_2$ with various difluorophosphine species. The reasoning behind the choice of this particular platinum species were three-fold. Firstly, if the first stage of reaction is indeed oxidative addition, then the potential exists to eliminate dihydrogen reductively. Such a step would block any further reaction and hopefully enable the detection of the desired product. Secondly, in the event of HCl being eliminated reductively, it was thought likely that the large bulk of the tricyclohexylphosphine groups would inhibit the formation of a bridged binuclear species. Thirdly, the air stability of this material simplifies the experimental procedures. The only disadvantage is the reduced solubility of this material compared with, say, $PtH_2(PEt_3)_2$[4,5], which is rather difficult to handle.

6.2. Reaction with F_2IP.

Reaction was rapid and at 190 K the $^{31}P-\{^1H\}$ n.m.r. spectrum showed a rather broad singlet with platinum satellites centered at +41.5 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. In addition to this, a wide, rather broad triplet, also with platinum satellites, was centered at +194 p.p.m. Raising the temperature to 190 K resulted in the lines of the low frequency resonance sharpening and showing a narrow doublet coupling which had been obscured by the line width. Similarly, all of the lines of the high frequency resonance showed narrow triplet coupling of the same size (fig.6.1). The chemical shift of the high frequency resonance was deemed to be far too low to be attributed to a terminal $-PF_2$ group by analogy with the value obtained for the iridium $-PF_2$ species[1] and the magnitude of the coupling to fluorine was indicative of a four-coordinate phosphorus. Retention of proton coupling broadened the tricyclohexyl phosphine resonance but had a substantial effect on the high frequency resonance (fig.6.2). The pattern was interpreted as being a triplet of doublets of doublets of triplets with platinum satellites. The additional couplings seemed to suggest that the platinum had a hydride trans to the unique phosphorus, which itself had a hydrogen directly bound to it. The ^1H nmr spectrum showed a complex low frequency hydride centered at -4.4 p.p.m. and a doublet

Fig. 6.1. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtH_2(PCy_3)_2$ + F_2IP at 190 K.

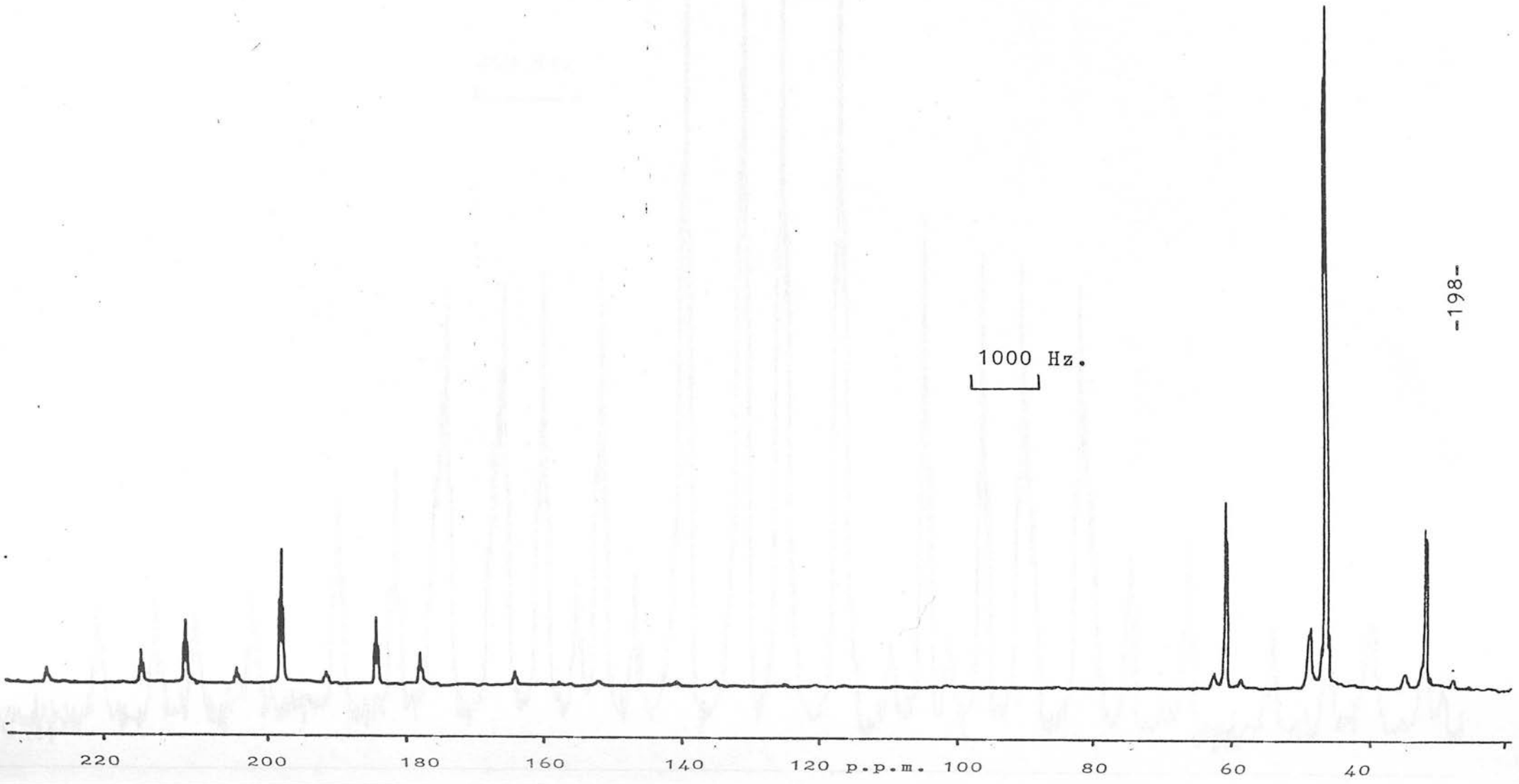
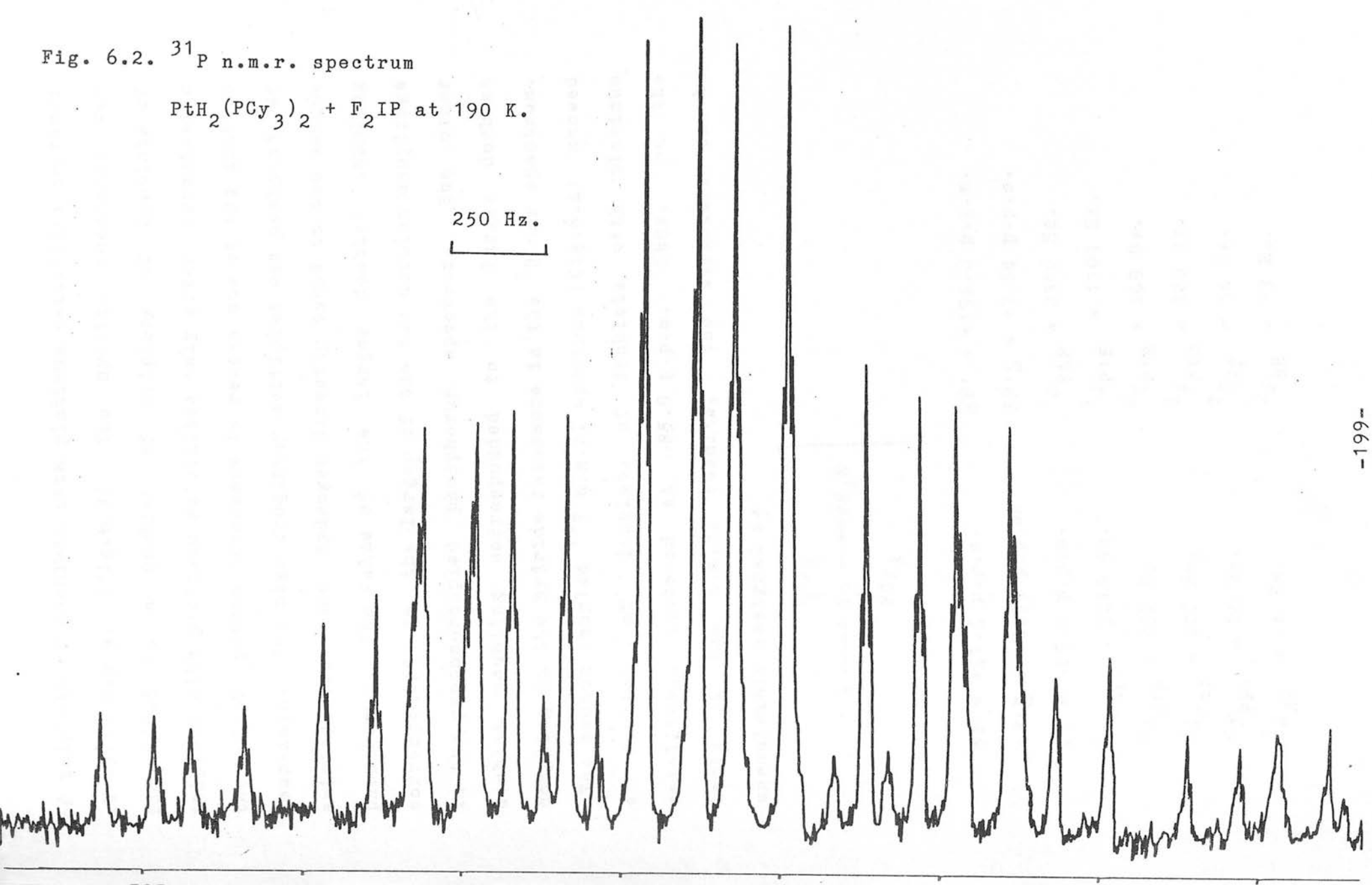
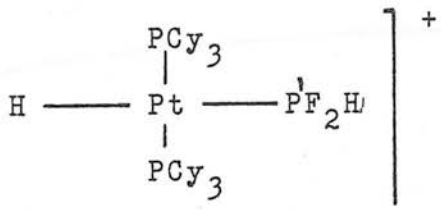


Fig. 6.2. ^{31}P n.m.r. spectrum

$PtH_2(PCy_3)_2$ + F_2IP at 190 K.



of triplets of doublets with platinum satellites centered at +9.59 p.p.m. (fig.6.3) The hydride resonance was identified as a doublet of triplets of doublets of triplets with platinum satellites only after irradiating the other proton resonance to remove one of the doublet couplings. The high frequency multiplet was assigned as arising from the hydrogen directly bound to the unique phosphorus. The value of the larger doublet coupling corresponded to the larger of the two doublet couplings in the proton-coupled phosphorus spectrum. The other doublet coupling corresponded to the larger doublet coupling in the hydride resonance in the ^{1}H nmr spectrum. The proton coupled ^{19}F n.m.r. spectrum (fig.6.4) showed a doublet of doublets of doublets with platinum satellites, centered at -85.9 p.p.m. Thus, on the basis of the n.m.r. results, the structure can be unequivably assigned as



$\delta P = +41.5$ p.p.m. $\quad \delta P' = +194.0$ p.p.m.

$\delta PtH = -4.39$ p.p.m. $\quad \delta P'H = +9.58$ p.p.m.

$\delta F = -85.9$ p.p.m. $\quad {}^{1}J_{PtP} = 2316$ Hz.

${}^{1}J_{PtP'} = 3219$ Hz. $\quad {}^{1}J_{P'F} = 1109$ Hz.

${}^{1}J_{P'H} = 452$ Hz. $\quad {}^{2}J_{P'H} = 269$ Hz.

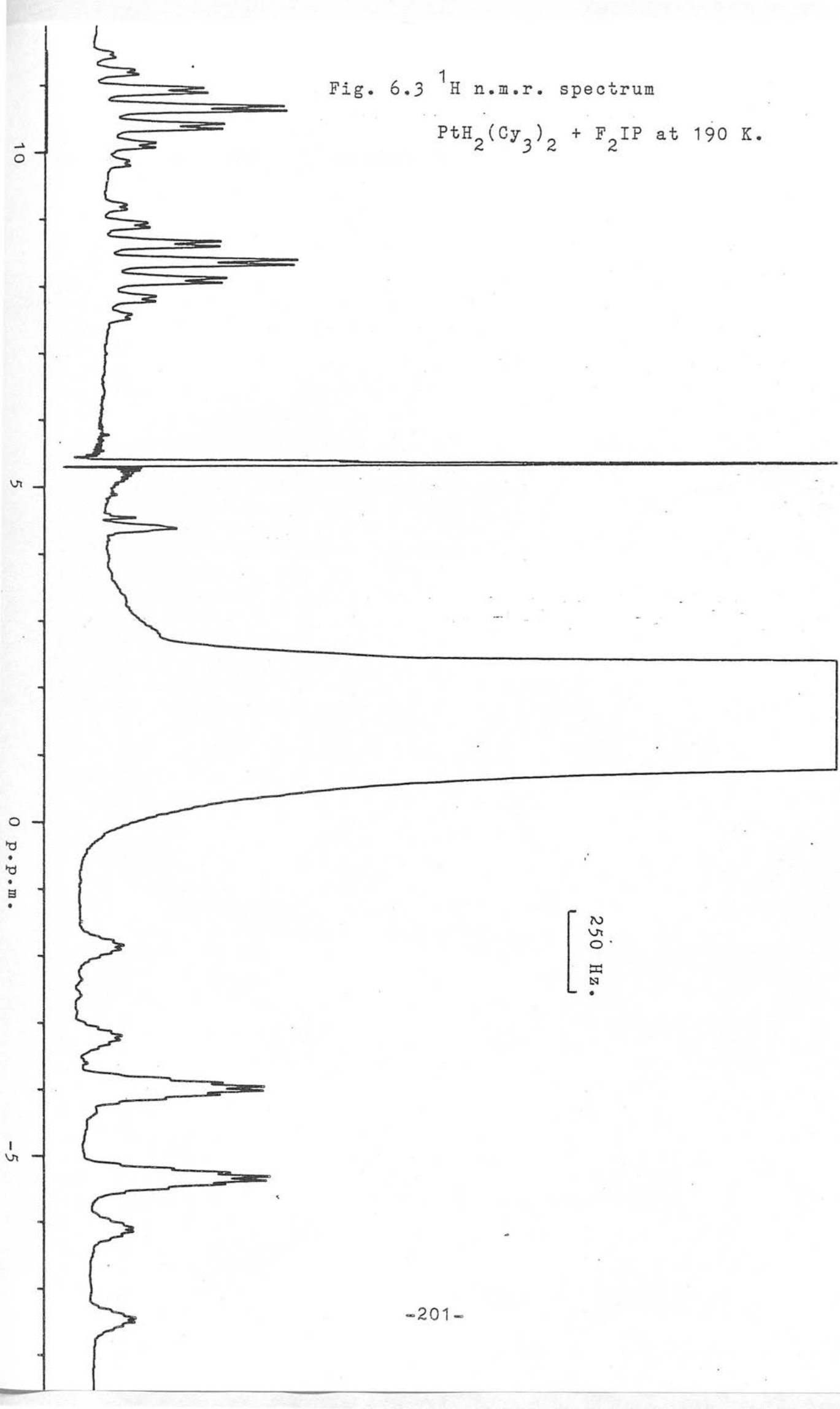
${}^{2}J_{PtF} = 220$ Hz. $\quad {}^{2}J_{PtH} = 220$ Hz.

${}^{2}J_{PP'} = 20$ Hz. $\quad {}^{2}J_{HF} = 54$ Hz.

${}^{3}J_{HF} = 26$ Hz. $\quad {}^{3}J_{HH} = 13$ Hz.

Fig. 6.3 ^{1}H n.m.r. spectrum

$PtH_2(Cy_3)_2$ + F_2IP at 190 K.



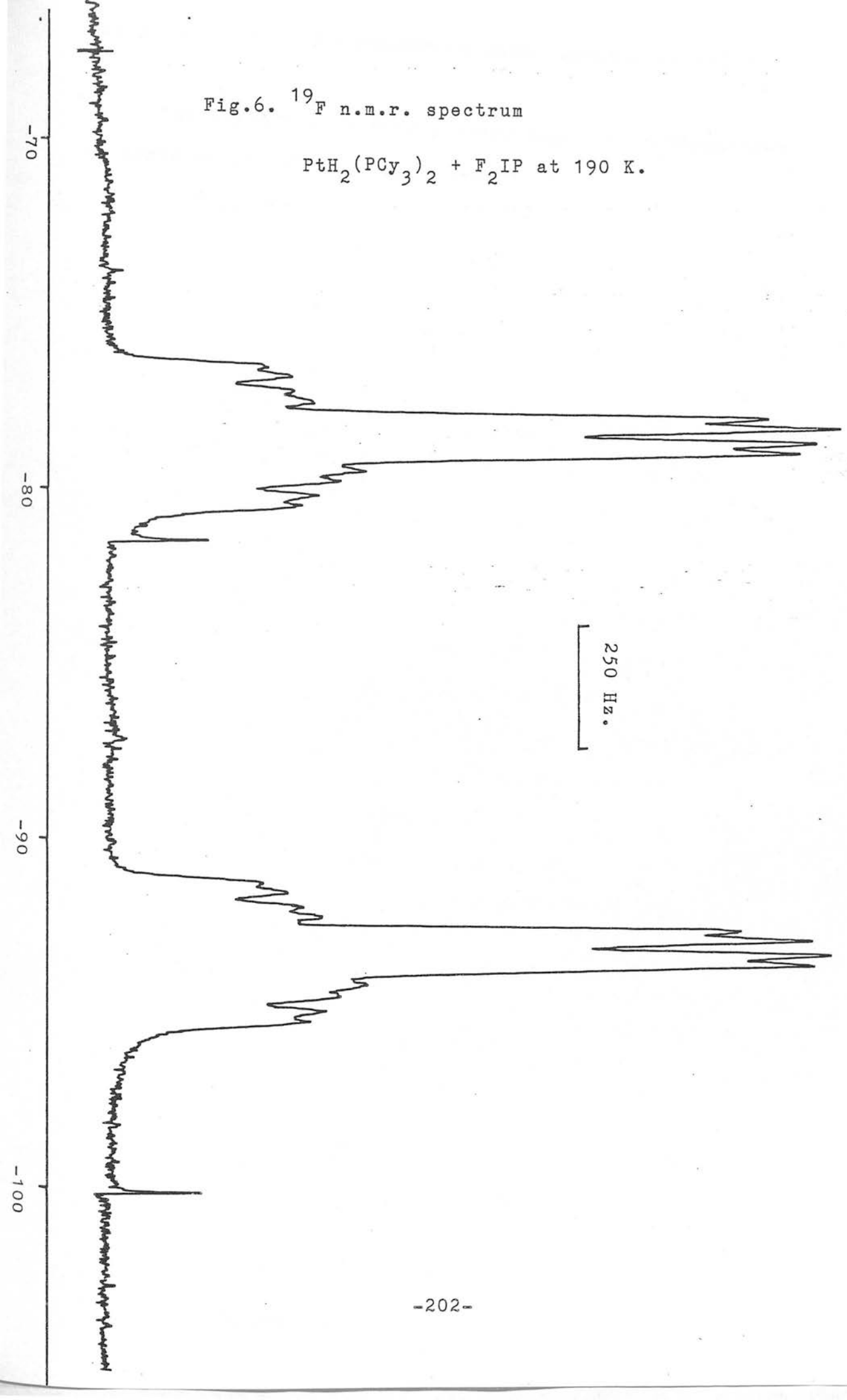
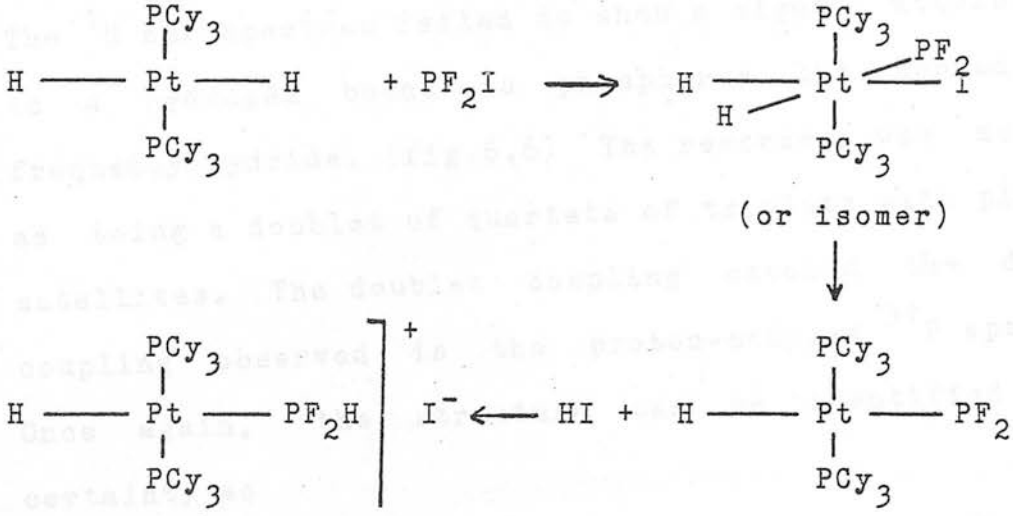


Fig.6. ^{19}F n.m.r. spectrum

$PtH_2(PCy_3)_2$ + F_2IP at 190 K.

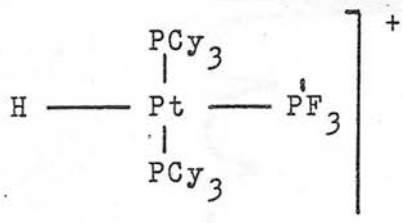
All parameters were recorded in dichlomethane at 190 K.

The formation of this species may be rationalised in terms of the following mechanism



Despite repeated attempts, it did not prove possible to detect either of the two intermediates proposed above. Further warming of the sample resulted in the appearance of small amounts of PF_3 and a new doublet with platinum satellites centered at +43.4 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. In the high frequency region, what initially appeared to be a wide doublet of triplets with platinum satellites partially overlapped the $-PF_2$ resonance of the cation described above. Whether the PF_3 arose from the decomposition of the cation or from the excess PF_2I present could not be determined. Warming the sample to 220 K resulted in an increase of the concentration of the new species at the expense of the initial cation. The structure of the high frequency resonance was now clearly a wide quartet of

triplets with platinum satellites. The large value of the phosphorus - fluorine coupling was indicative of a coordinated PF_3 group. Retention of proton coupling resulted in a further wide doublet coupling. (fig.6.5.) The ^1H nmr spectrum failed to show a signal attributable to a hydrogen bound to phosphorus but showed a low frequency hydride. (fig.6.6) The resonance was assigned as being a doublet of quartets of triplets with platinum satellites. The doublet coupling matched the doublet coupling observed in the proton-coupled ^{31}P spectrum. Once again, the structure can be identified with certainty as



$\delta P = +43.4$ p.p.m. $\quad \delta P' = +138.2$ p.p.m.

$\delta F = -26.1$ p.p.m. $\quad \delta H = -3.21$ p.p.m.

$^1J_{PtP} = 2234$ Hz. $\quad ^1J_{PtP'} = 3362$ Hz.

$^1J_{P'F} = 1359$ Hz. $\quad ^2J_{P'H} = 351$ Hz.

$^2J_{PP'} = 22$ Hz. $\quad ^2J_{PH} = 12$ Hz.

$^2J_{PtF} = 356$ Hz. $\quad ^3J_{FH} = 48$ Hz.

$^3J_{PF}$ = n.o.

n.o. means not observed.

All parameters were recorded in dichlomethane at 220 K.

The counter-anion was assumed to be iodide in the absence of any realistic alternative. As direct reaction of PF_3 fails to produce this cation, it must arise

Fig. 6.5. ^{31}P n.m.r. spectrum $PtH_2(PCy_3)_2$ + F_2IP at 220 K.

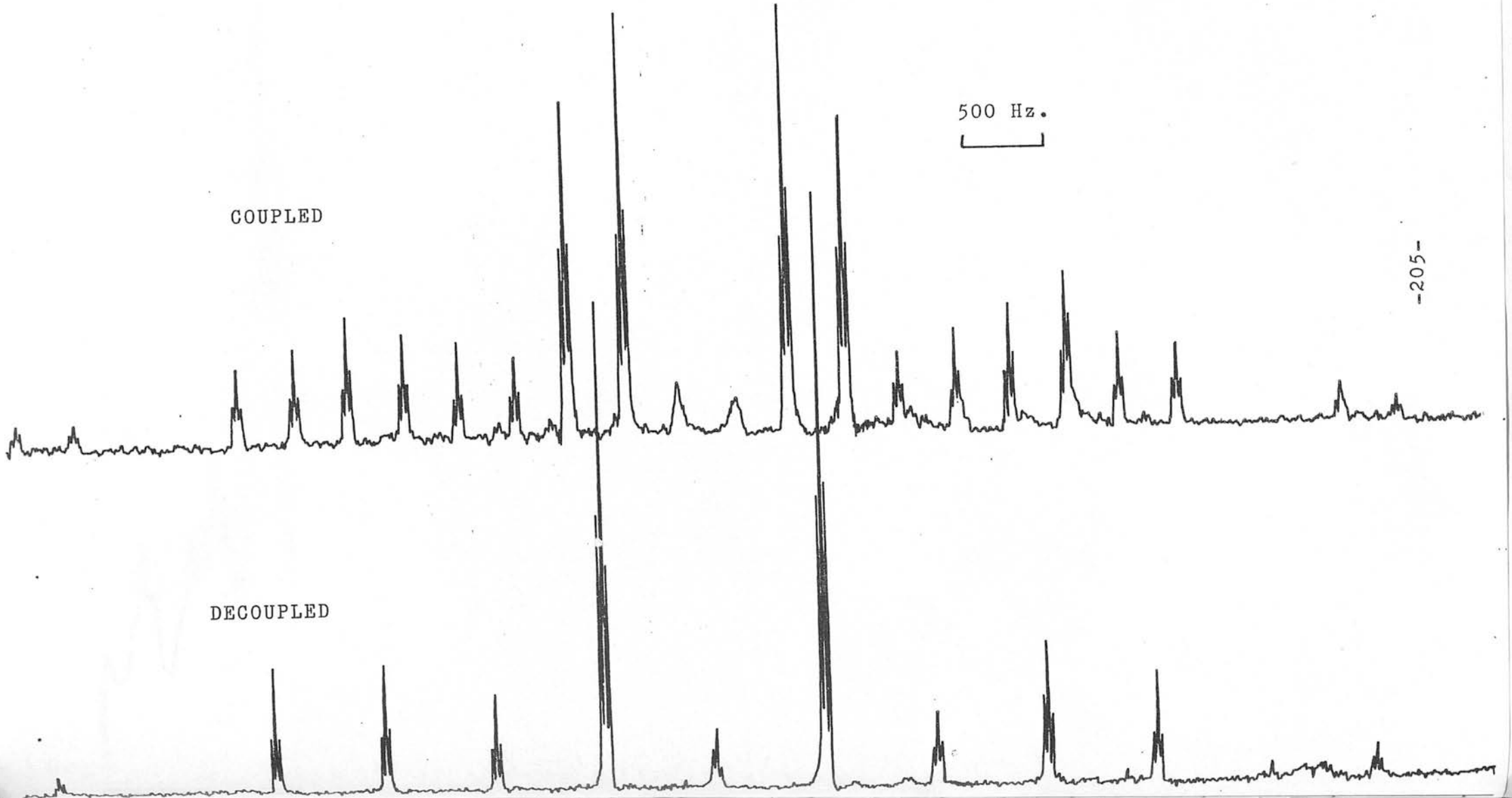
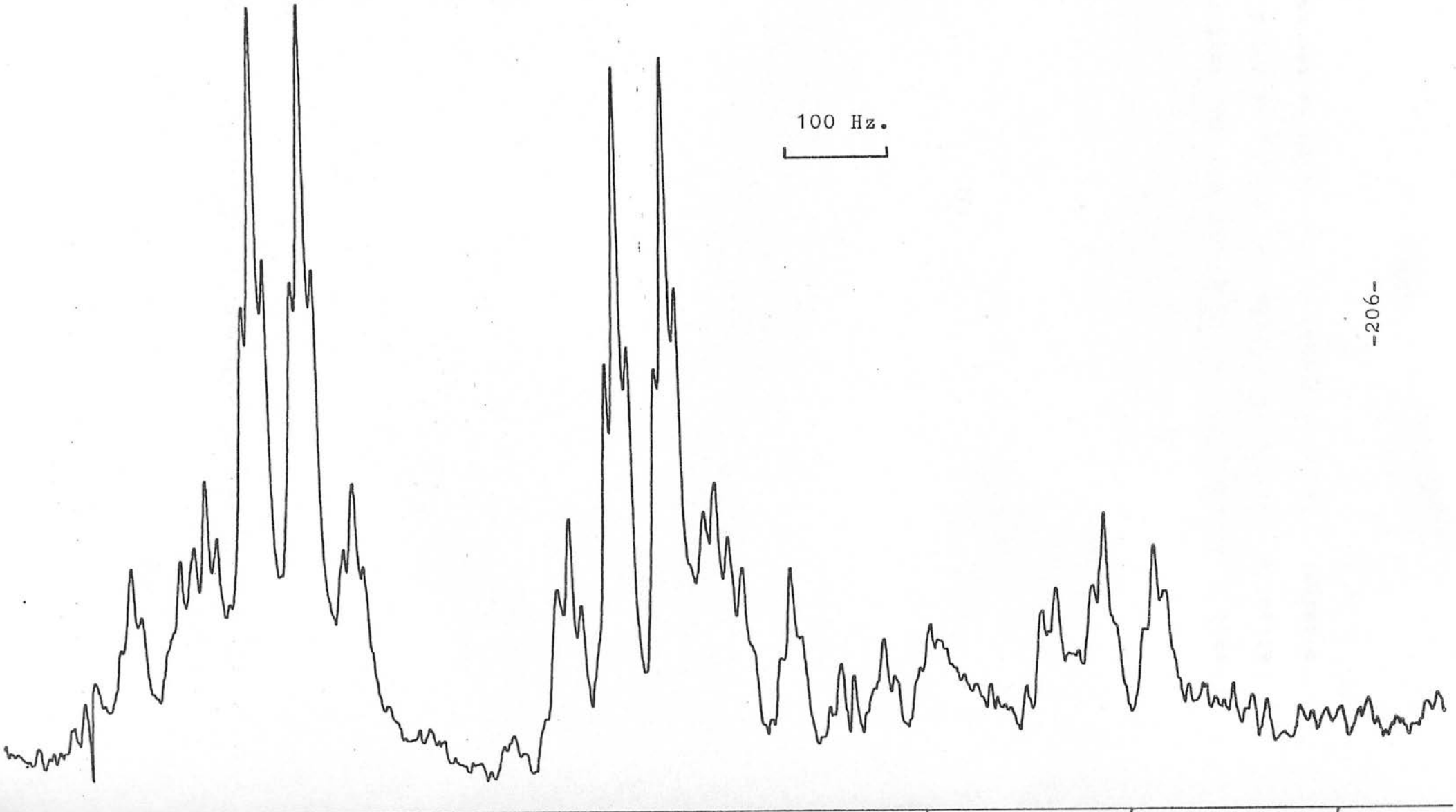


Fig. 6.6. ^{1}H n.m.r. spectrum $PtH_2(PCy_3)_2$ + F_2IP at 220 K.



either from rearrangement of the $-PF_2H$ cation at the unique phosphorus centre or by reaction of PF_3 with the $-PF_2H$ cation. Further warming the sample towards ambient temperature resulted in the gradual decomposition of the products to leave a species identified as $PtHI(PCy_3)_2$ on the basis of its n.m.r. parameters.[6]

6.3. Reaction with PF_2X (X = Cl or Br).

Reaction with either of these reagents produced the same initial cationic product as found in the reacion with PF_2I and further warming resulted in the formation of the same $-PF_3$ cation. Presumably, the counter anions were chloride and bromide respectively but the n.m.r. parameters were the same as those obtained previously. The only difference was in the rate at which the initial product was converted into the second. The rate of this reaction was found to be faster, and occurred at lower temperature, the higher the weight of halogen in the difluorophosphine. This tends to suggest that the mechanism proceeds via reaction of PF_3 with the coordinated $-PF_2H$ ligand since PF_2I decomposes the most readily to give PF_3 as one of the products. Had the mechanism involved an intramolecular rearrangement at the unique phosphorus centre, then the identity of the counter anion would not be expected to have a significant effect on the rate of the reaction. In order to check this hypothesis, the PF_2H cation was preformed by allowing PF_2Cl to react with $PtH_2(PEt_3)_2$ at 200 K for 10 minutes. Two equivalents of PF_3 (based on the amount of

platinum initially used) was added at 77 K. The resulting $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 190 K showed the PF_3 cation to be the major product. In the reaction between PF_2Cl and $PtH_2(PEt_3)_2$ the solution had to be warmed to a temperature of about 230 K before the PF_3 complex was obtained. Further warming of these systems resulted in the decomposition of the product in a similar manner to that observed for the reaction involving PF_2I.

6.4. Reaction of $PtH_2(PCy_3)_2$ with PF_2X in toluene.
(X = Cl, Br & I)

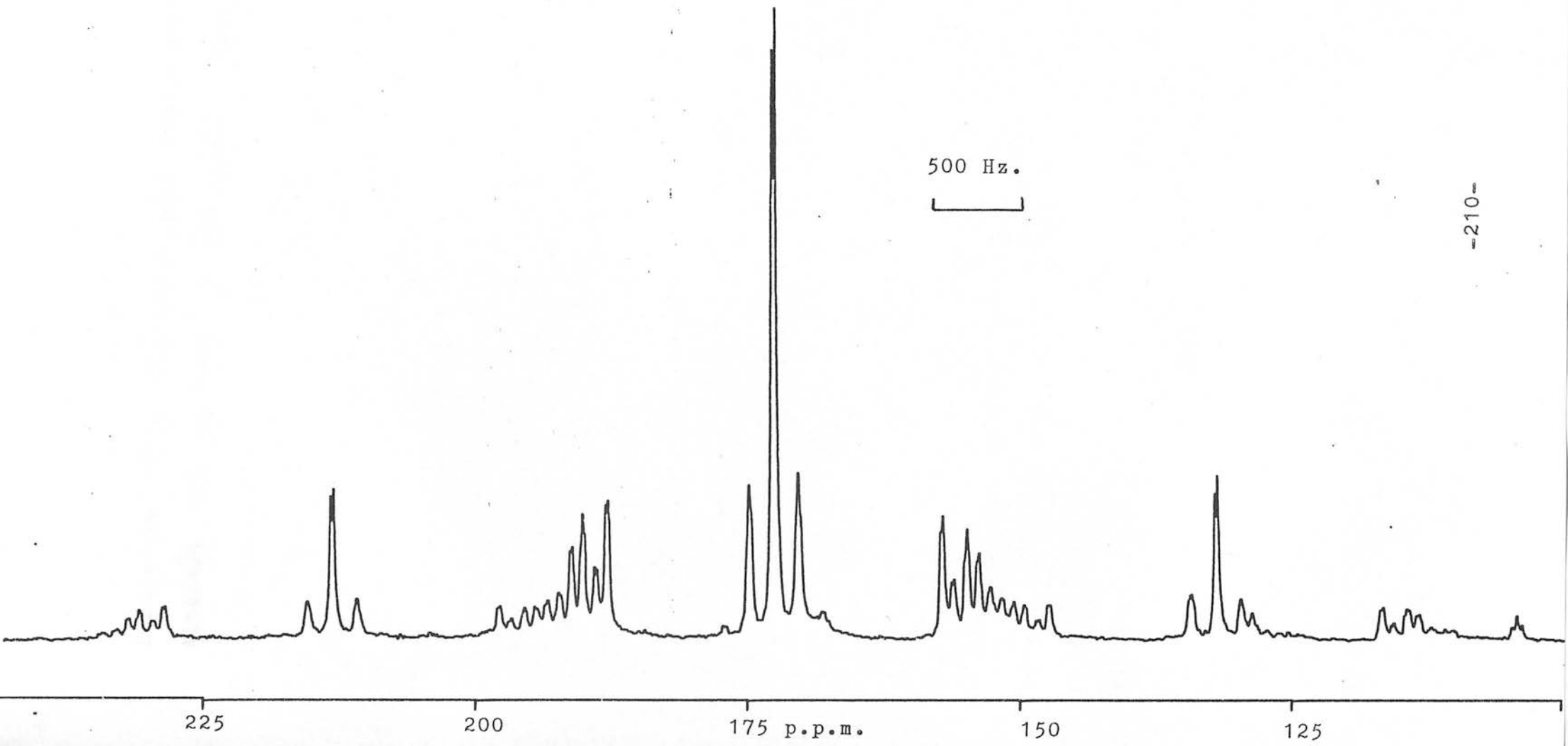
In an attempt to discourage the formation of the cationic $-PF_2H$ species, it was decided to carry out the reaction in toluene which tends to be a poorer solvent for ionic species and so might result in the reductive elimination of dihydrogen rather then hydrogen chloride. Failing this, the less polar solvent might result in a longer lifetime of one of the intermediate species postulated earlier.

Reaction with PF_2I resulted in a very rapid reaction as soon as the solvent melted. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 176 K showed a broad triplet, apparently without platinum satellites, centered at +316 p.p.m. A slightly broadened singlet with platinum satellites was centered at +42.4 p.p.m. The magnitude of the coupling to platinum was indicative of a four-coordinate platinum(II) species. The only other resonances detected were attributable to $PtH_2(PCy_3)_2$. The chemical shift of the high frequency resonance is

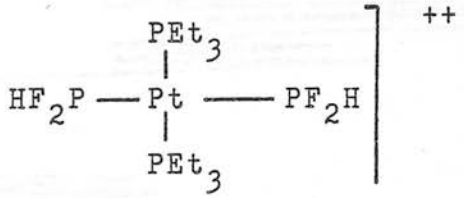
lower than would be expected for a terminal $-PF_2$ group by analogy with the iridium case. The coupling to fluorine, however was indicative of three-coordinate phosphorus. Retention of proton coupling had no effect on this resonance but broadened the low frequency signals. Attempts to obtain a proton spectrum were unsuccesful due to the amount of undissolved material at this temperature and the slight fizzing of the solution. Similar problems prevented a good quality $^{19}F-\{^1H\}$ n.m.r. spectrum being obtained. Both of these sets of phosphorus resonances dissapeared at the same time after about 30 minutes at 176 K. Whether this species was indeed the elusive terminal $-PF_2$ complex cannot be determined. The apparent absence of platinum satellites on the high frequency resonance could be explained if the coupling to platinum was of the same order as that observed in the case of the analogous $-PCl_2$ species.

Raising the temperature to 180 K resulted in the appearance of a complex second order pattern centered at +175 p.p.m. in the $^{31}P-\{^1H\}$ n.m.r. spectrum (fig.6.7). The spin system was recognised as an $(AX_2)_2M$ type with additional couplings present, presumably due to first order coupling to two tricyclohexyl phosphine ligands, the M component arising from the platinum coupling. Due to the the second order nature of this resonance it was not possible to measure any parameters directly from the spectrum. Both the ^1H and the $^{19}F-\{^1H\}$ n.m.r. spectra were hopelessly broad and no information could be obtained at this temperature. A broad singlet with

Fig. 6.7. $^{31}P-\{^{1}H\}$ n.m.r. spectrum $PtH_2(PCy_3)_2$ + F_2IP in toluene at 180 K.



platinum satellites was centered at +40.2 p.p.m. in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. The coupling to platinum was indicative of a four-coordinate platinum(II) species. Although the contents of the n.m.r. tube were now completely dissolved, the solution was extremely viscous and the spectra took large numbers of accumulations to achieve acceptable signal to noise ratios. Raising the temperature to 230 K improved this problem sufficiently that the proton-coupled phosphorus spectrum was obtained after three hours of accumulating (fig.6.8). Once again the spectrum was complex and second order but was recognised as arising from a $(AHX_2)_2M$ system[7] with additional coupling from two other A' nuclei in a first order manner. This implies that the molecule contains two trans tricyclohexyl phosphine ligands and two $-PF_2H$ ligands.

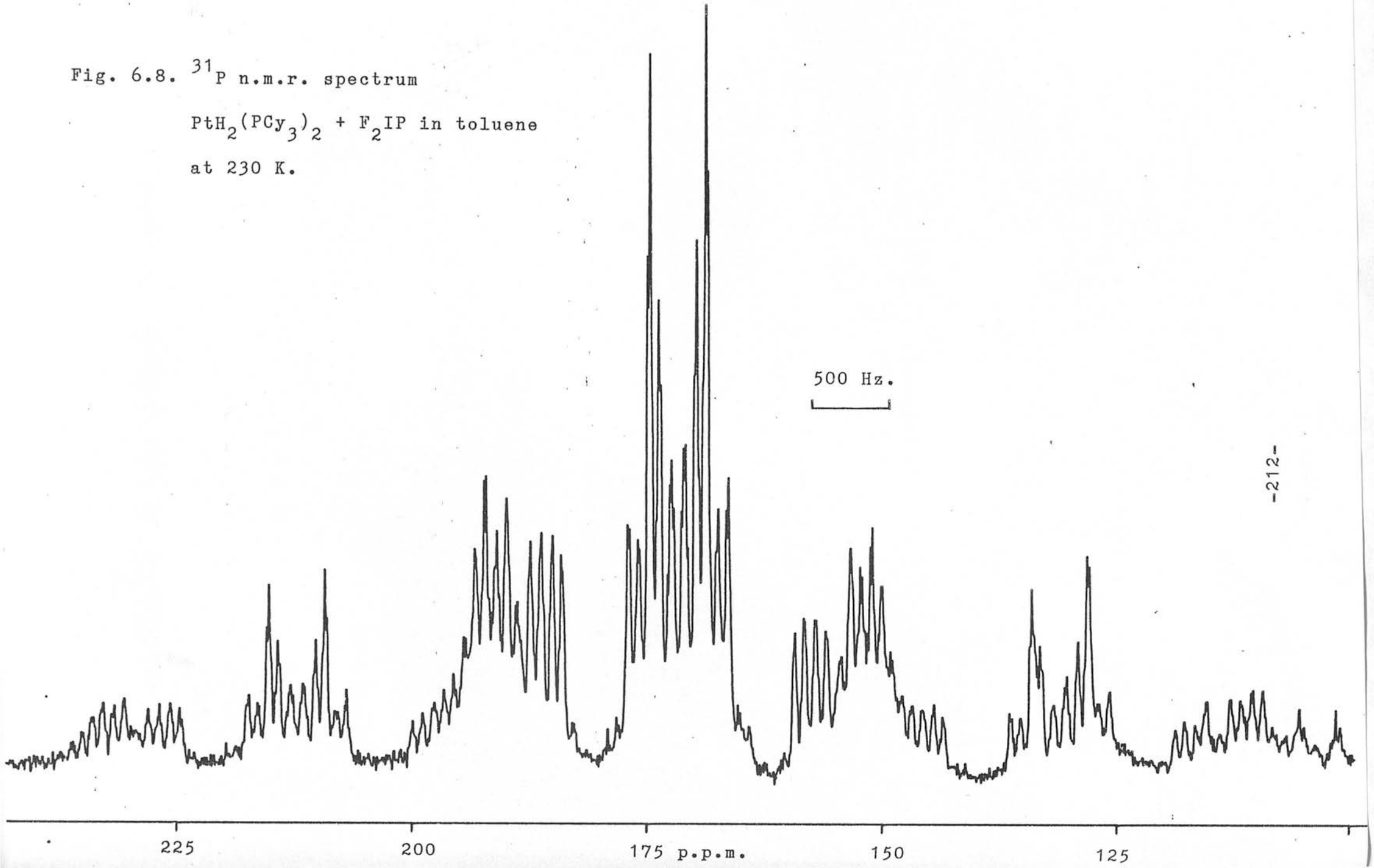


The counter anions were presumed to be iodide. The $^{19}F-\{^{1}H\}$ n.m.r. spectrum showed some detail but the line widths were of the order of 200 Hz. This was rather surprising considering the sharpness of the lines in the phosphorus spectrum. Running the sample on a higher field instrument made the problem even worse and no detail whatsoever could be observed. Further warming of the sample resulted in the decomposition of this species to leave so much orange solid in the tube that no further spectra could be obtained. Repeating the reaction

Fig. 6.8. ^{31}P n.m.r. spectrum

$PtH_2(PCy_3)_2$ + F_2IP in toluene

at 230 K.



resulted in identical behaviour and no better spectra could be obtained. Without a good quality $^{19}F-\{^{1}H\}$ n.m.r. spectrum it is not possible to obtain enough information to undertake a simulation of the phosphorus spectrum which is the only way to establish the parameters for the product.

Repeating the reaction using either PF_2Cl or PF_2Br gave an apparently identical product but failed to show the very low temperature species. Again the problems in obtaining fluorine spectra could not be overcome. At this time it was decided to try other routes to produce a terminal $-PF_2$ containing species.

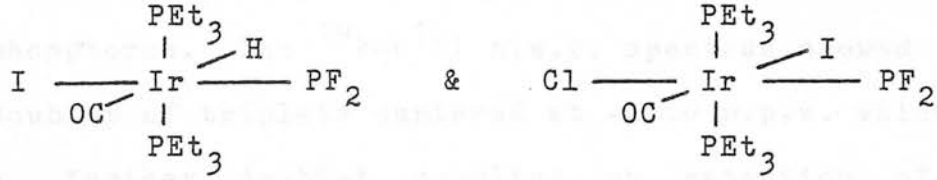
6.5. Attempts to deprotonate $[PtH(PCy_3)_2(PF_2H)]^+I^-$.

Acting on the assumption that the unique phosphorus was protonated in the course of the formation of the title compound, it was decided to attempt to deprotonate it with base. The cation was allowed to form by reaction of $PtH_2(PCy_3)_2$ with PF_2I in CD_2Cl_2 in an n.m.r.tube at 200 K for 30 minutes. One equivalent of trimethylamine, based on the amount of platinum used, was then added at 77 K and the tube sealed. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 176 K showed no starting cation whatsoever but the rapid, and fairly clean, formation of the $-PF_3$ cation. No further reaction was observed until this species decomposed as the temperature was raised. Similar results were obtained when di- and monomethylamines were used. Reaction with butyllithium in diethylether

resulted in the decomposition of all platinum species as soon as the solvent melted.

Due to the failure of conventional bases to achieve the desired deprotonation, it was decided to study the reaction with two iridium(I) species which have shown a strong tendency to abstract HX, - $IrCl(CO)(PEt_3)_2$ and $Ir(CO)H(PPh_3)_3$

The $-PF_2H$ cation was preformed as described in the previous section and one equivalent of $IrCl(CO)(PEt_3)_2$ added under nitrogen at 77 K as described previously. As soon as the solvent melted the $^{31}P-\{^1H\}$ n.m.r. spectrum showed two high frequency triplets, neither of which showed platinum satellites. Corresponding doublet resonances were located in the region around zero, again without satellites. Comparison with work carried out in this department[8] allowed the species to be identified as



These species were previously prepared by the reactions of $Ir(CO)I(PEt_3)_2$ with HPF_2 and $IrCl(CO)(PEt_3)_2$ with PF_2I respectively. Thus the formation of the latter can be explained by the presence of excess PF_2I in the system. The former product however cannot be explained in such a simple manner. Presumably, some sort of exchange process with the $-PF_2H$ cation has made PF_2H available for reaction with the iridium chloride and halogen exchange with the iodide ions present results in

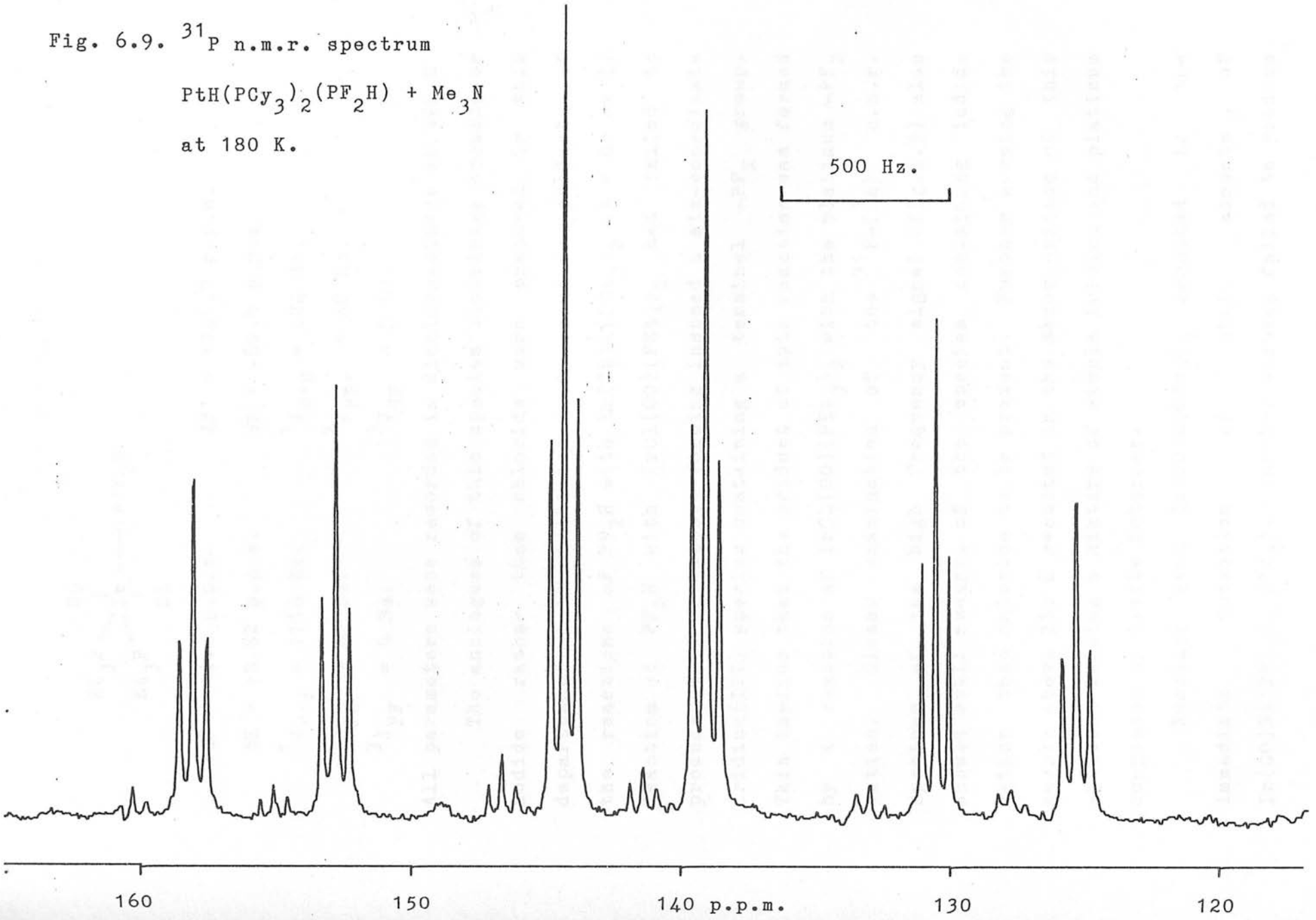
the product observed. As no evidence was found for the presence of free PF_2H in the system, it must be assumed that it was derived from the platinum species.

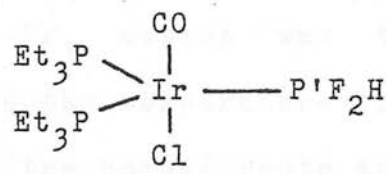
Further warming the sample to 190 K resulted in the loss of the resonances associated with the former of these two products and the latter species decomposed on raising the temperature to 210 K. The $^{31}P-\{^1H\}$ n.m.r. spectrum at 220 K showed a high frequency triplet without platinum satellites centered at +141.7 p.p.m. A doublet of narrow triplets centered at +4.6 p.p.m. was also detected. The size of the doublet coupling in this resonance was the same as the triplet coupling in the high frequency resonance. Retention of proton coupling resulted in the broadening of the low frequency resonance but the high frequency signal split into a further wide doublet (fig.6.9). The magnitude of the coupling was indicative of hydrogen directly bound to four-coordinate phosphorus. The $^{19}F-\{^1H\}$ n.m.r. spectrum showed a wide doublet of triplets centered at -60.0 p.p.m. which showed a further doublet coupling on retention of proton coupling. The ^1H nmr spectrum failed to show a low frequency hydride but showed a wide doublet of triplets of triplets centered at +8.82 p.p.m., assigned as arising from the proton attached to the unique phosphorus. The phosphorus chemical shift of the triethylphosphine resonance suggested the species to contain an iridium(I) centre and, by comparison with similar species, the structure was assigned as

Fig. 6.9. ^{31}P n.m.r. spectrum

$PtH(PCy_3)_2(PF_2H)$ + Me_3N

at 180 K.





$\delta P = +4.6$ p.p.m. $\quad \delta P' = +141.7$ p.p.m.

$\delta H = +8.82$ p.p.m. $\quad \delta F = -60.0$ p.p.m.

$^1J_{P'F} = 1116$ Hz. $\quad ^1J_{P'H} = 424$ Hz.

$^2J_{FH} = 61$ Hz. $\quad ^2J_{PP'} = 40$ Hz.

$^3J_{PF} = 6$ Hz. $\quad ^3J_{HP} = 5$ Hz.

All parameters were recorded in dichloromethane at 220 K

The analogues of this species containing bromide or iodide rather than chloride were prepared in this department[8] as the initial low temperature products of the reactions of PF_2H with $Ir(CO)X(PEt_3)_2$ (X = Br or I) Reaction of PF_2H with $IrCl(CO)(PEt_3)_2$ had failed to produce this species, forming instead a six-coordinate iridium(III) species containing a terminal $-PF_2$ group. This implies that the product of this reaction was formed by a reaction of $IrCl(CO)(PEt_3)_2$ with the platinum $-PF_2$ cation. Closer examination of the $^{31}P-\{^1H\}$ n.m.r. spectrum of the high frequency signal (fig.6.9) also showed small amounts of the species containing iodide rather than chloride to be present. Further warming the sample above 250 K resulted in the decomposition of this species leaving a mixture of simple iridium and platinum complexes of little interest.

Reaction with $Ir(CO)H(PPh_3)_3$ resulted in the immediate formation of small amounts of $Ir(CO)HI(PEt_3)_2(P'F_2)$. Further warming failed to produce

any other new iridium species and large amounts of the platinum-PF_3 cation was the only new platinum species formed as the temperature inceased. Decomposition took place by the normal route and no further work was carried out on this system.

6.6. Reaction of $PtH_2(PCy_3)_2$ with PF_2I in the presence of trimethylamine.

The failure to deprotonate the $-PF_2H$ cation was, in retrospect, not as difficult to explain as was first thought. Recent work in this department[9] has produced a six-coordinate iridium(III) species which contains a hydride trans to a $-PH_2$ group. Experiments have shown that this $-PH_2$ group is approximately as basic as a tertiary ammine. By analogy, a $-PF_2$ group trans to a hydride may also be unexpectadely basic in character. This would result in it protonating very readily and the resulting $-PF_2H$ group being very tightly held together. A $-PH_2$ trans to a chlorine however is not particularly basic in nature. On this basis, the answer is to attempt to produce a reaction in which the intermediate terminal $-PF_2$ species has a halogen trans to the $-PF_2$ group. Unfortunately there is no reaction between $PtClH(PCy_3)_2$ and PF_2I. The alternative is to remove the eliminated HX before it has a chance to protonate the $-PF_2$ group. By analogy with the synthesis of $PtCl(PEt_3)_2(PCl_2)$, the reaction between $PtH_2(PCy_3)_2$ and PF_2I was carried out in the presence of a stoichiometric amount of trimethylamine. The resultant $^{31}P-\{^1H\}$ n.m.r.

spectrum at 176 K showed very small amounts of the $-PF_2H$ cation but the major product was the PF_3 cation. No other products were observed before decomposition occurred by the normal route.

Once again, attempts to synthesise, or even observe, the elusive terminal $-PF_2$ group on a platinum centre have failed. Further work will have to be performed in order to produce this potentially very interesting species.

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APPENDIX

N.M.R. PARAMETERS OF SOME PHOSPHINE COMPLEXES OF IRIDIUM, PLATINUM & RHODIUM.

Throughout the course of this work, fairly simple transition-metal reactions were prone to producing large numbers of common species, either as intermediates, or more commonly as decomposition products. Although current literature reports ^{31}P n.m.r. data as a matter of routine, when these simple species were first reported, this practise was not common. Reports of phosphorus, and even more so platinum, n.m.r. parameters were less common and tended to be derived from double resonance experiments.

For this reason, it was decided to prepare samples of the commonly encountered complexes of iridium, platinum and rhodium and record the relevant spectra using dichloromethane as solvent. All of the species reported contain tertiary phosphines in keeping with the research carried out in this section of the department. The preparations of some of these complexes can be found in chapter 2 of this work, the remainder are well documented in the literature.

It is to be stressed that no attempt is being made to rationalise these parametrs, merely to present a usefull collection of numbers.

Chemical shifts are in p.p.m., positive to high frequency of the standards described in chapter 2. Coupling constants are in Hz.

TABLE A.1.

N.m.r. parameters for some Platinum(II) species.

	P	$^1J_{PtP}$	Pt	OTHERS
t-$PtClH(PEt_3)_2$	+23.0	2710	0	H = -16.8 $^1J_{PtH}$ = 1275
t-$PtBrH(PEt_3)_2$	+21.8	2679	-126	H = -15.6 $^1J_{PtH}$ = 1331
t-$PtIH(PEt_3)_2$	+19.5	2638	-325	H = -12.6 $^1J_{PtH}$ = 1369
t-$PtCl_2(PEt_3)_2$	+12.3	2457	+946	
t-$PtBr_2(PEt_3)_2$	+7.6	2368	+384	
t-$PtI_2(PEt_3)_2$	+0.2	2272	-672	
c-$PtCl_2(PEt_3)_2$	+9.2	3505	+414	
c-$PtBr_2(PEt_3)_2$	+8.3	3475	+214	
c-$PtI_2(PEt_3)_2$	+6.7	3372	-407	
$Pt_2Cl_4(PEt_3)_2$	+11.2	3843	+1105	$^3J_{PtP}$ = 22
$Pt_2I_4(PEt_3)_2$	+9.9	3510	-803	$^3J_{PtP}$ = 24
t-$PtH_2(PCy_3)_2$	+51.8	2837	-846	H = -3.9 $^1J_{PtH}$ = 796
t-$PtClH(PCy_3)_2$	+38.5	2802	-266	H = -18.7 $^1J_{PtH}$ = 1279

All spectra were recorded in dichloromethane at 298 K

Coupling constants $\pm$ 1.0 Hz.

Chemical shifts $\pm$0.05 except ^{195}Pt $\pm$ 1.0 p.p.m.

TABLE A.2.

N.m.r. parameters for some ionic platinum(II) and neutral platinum(IV) species.

	P	$^1J_{PtP}$	Pt	OTHERS
$^*[PtCl_3(PEt_3)]^-$	+1.8	3703	+1006	
$^*[PtBr_3(PEt_3)]^-$	+1.6	3581	+378	
$^*[PtI_3(PEt_3)]^-$	+1.9	3427	-1015	
$[PtH(PEt_3)_3]^+\phi$	+16.7[a]	2515	-586	H = -6.1 $^2J_{PtH}$ = 787
	+13.9[b]	2050		$^2J_{PP'}$ = 21
$[PtCl(PEt_3)_3]^+\phi$	+18.8[a]	2260	-190	$^2J_{PP'}$ = 10
	+9.8[b]	3477		
$[PtBr(PEt_3)_3]^+\phi$	+14.8[a]	2248	-281	$^2J_{PP'}$ = 14
	+10.8[b]	3475		
$[PtI(PEt_3)_3]^+\phi$	+9.2[a]	2247	-437	$^2J_{PP'}$ = 18
	+7.1[b]	3376		
$PtCl_2H_2(PEt_3)_2$	+12.2	1769	+881	H = -16.9 $^1J_{PtH}$ = 1176
$PtBr_2H_2(PEt_3)_2$	+7.2	1710	+534	H = -18.2 $^1J_{PtH}$ = 1204
$PtI_2H_2(PEt_3)_2$	-1.4	1728	-146	H = -19.0 $^1J_{PtH}$ = 1186

All parameters were recorded in dichloromethane at 298 K

a = doublet signal arising from the pair of phosphines.

b = triplet signal arising from the unique phosphorus.

$^* = [Pr_4N]^+$ $\phi = [BPh_4]^-$

Coupling constants $\pm$1.0 Hz.

Chemical shifts $\pm$0.05 except ^{195}Pt $\pm$1.0 p.p.m.

The geometry of the six-coordinate species was cis-cis-trans-

TABLE A.3.

N.m.r. parameters for some Iridium species.

	P	H
$IrCl(CO)(PEt_3)_2$	+20.0	-
$IrBr(CO)(PEt_3)_2$	+17.3	-
$IrI(CO)(PEt_3)_2$	+13.4	-
$IrCl_2(CO)H(PEt_3)_2$	-1.3	-16.9
$IrBr_2(CO)H(PEt_3)_2$	-6.6	-16.1
$IrI_2(CO)H(PEt_3)_2$	-8.2	-15.0

All parameters were recorded in dichloromethane at 298 K

Coupling constants $\pm$1.0 Hz.

Chemical shifts $\pm$0.05 p.p.m.

TABLE A.4.

N.m.r. parameters for some Rhodium species.

	P	H	$^1J_{RhP}$	$^1J_{RhH}$
$RhCl(CO)(PEt_3)_2$	+29.1	-	124	
$RhBr(CO)(PEt_3)_2$	+22.2	-	115	
$RhI(CO)(PEt_3)_2$	+19.9	-	114	
$RhCl_2(CO)H(PEt_3)_2$	26.7	-13.4	81	17
$RhBr_2(CO)H(PEt_3)_2$	19.4	-12.6	78	17
$RhI_2(CO)H(PEt_3)_2$	13.7	-12.1	80	16

All parameters were recorded in dichloromethane at 298 K

Coupling constants $\pm$1.0 Hz.

Chemical shifts $\pm$0.05. p.p.m.

LIST OF COURSES ATTENDED.

Attendance at U.S.I.C. conference - four years.	
Applications of synchrotron radiation.	Staff of Daresbury research laboratories.
Homogeneous catalysis.	Dr.T.A.Stephenson.
F.T. infra-red spectroscopy.	Drs. S.Craddock, J.Duncan & A.Morrison.
Inorganic Cluster chemistry.	Dr.A.J.Welch.
Aspects of structural chemistry.	Dr.C.Glidewell.
Modern inorganic chemistry.	Prof.E.A.V.Ebsworth & D.S.Craddock.
Applications of microcomputers.	Dr.A.G.Rowley & Mr.A.King.
N.m.r. spectroscopy.	Dr.I.H.Sadler.
Lasers in chemistry.	Prof.R.J.Donovan & Dr.C.Fotakis.